

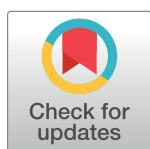
RESEARCH ARTICLE

Green synthesis of SiO₂ nanoparticles from Rhus coriaria L. extract: Comparison with chemically synthesized SiO₂ nanoparticles

Chiya Yousef Rahimzadeh^{1,2*}, Azeez Abdullah Barzinjy^{3,4*}, Ahmed Salih Mohammed⁵, Samir Mustafa Hamad^{1,6}

1 Scientific Research Centre, Soran University, Soran, Kurdistan-Region, Iraq, **2** Civil Engineering Department, Faculty of Engineering, Soran University, Soran, Kurdistan-Region, Iraq, **3** Department of Physics, College of Education, Salahaddin University-Erbil, Erbil, Kurdistan-Region, Iraq, **4** Department of Physics Education, Faculty of Education, Tishk International University, Erbil, Kurdistan-Region, Iraq, **5** Civil Engineering Department, College of Engineering, University of Sulaimani, Kurdistan, Iraq, **6** Computer Department, Cihan University-Erbil, Erbil, Iraq

* azeez.azeez@su.edu.krd (AAB); chiya.yousef@soran.edu.iq (CYR)



OPEN ACCESS

Citation: Rahimzadeh CY, Barzinjy AA, Mohammed AS, Hamad SM (2022) Green synthesis of SiO₂ nanoparticles from Rhus coriaria L. extract: Comparison with chemically synthesized SiO₂ nanoparticles. PLoS ONE 17(8): e0268184. <https://doi.org/10.1371/journal.pone.0268184>

Editor: Amitava Mukherjee, VIT University, INDIA

Received: January 28, 2022

Accepted: April 25, 2022

Published: August 5, 2022

Peer Review History: PLOS recognizes the benefits of transparency in the peer review process; therefore, we enable the publication of all of the content of peer review and author responses alongside final, published articles. The editorial history of this article is available here: <https://doi.org/10.1371/journal.pone.0268184>

Copyright: © 2022 Rahimzadeh et al. This is an open access article distributed under the terms of the [Creative Commons Attribution License](https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Data Availability Statement: No

Funding: The authors received no specific funding for this work.

Abstract

The usage of the green synthesis method to produce nanoparticles (NPs) has received great acceptance among the scientific community in recent years. This, perhaps, is owing to its eco-friendliness and the utilization of non-toxic materials during the synthesizing process. The green synthesis approach also supplies a reducing and a capping agent, which increases the stability of the NPs through the available phytochemicals in the plant extractions. The present study describes a green synthesis method to produce nano-silica (SiO₂) NPs utilizing Rhus coriaria L. extract and sodium metasilicate (Na₂SiO₃·5H₂O) under reflux conditions. Sodium hydroxide (NaOH) is added to the mixture to control the pH of the solution. Then, the obtained NPs have been compared with the chemically synthesized SiO₂ NPs. The structure, thermal, and morphological properties of the SiO₂ NPs, both green synthesized and chemically synthesized, were characterized using Fourier-transform infrared spectroscopy (FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis), X-ray diffraction (XRD), and Field Emission Scanning Electron Microscopy (FESEM). Also, the elemental composition distribution was studied by energy-dispersive X-ray spectroscopy (EDX). In addition, the zeta potential, dynamic light scatter (DLS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) was used to study the stability, thermal properties, and surface area of the SiO₂ NPs. The overall results revealed that the green synthesis of SiO₂ NPs outperforms chemically synthesized SiO₂ NPs. This is expected since the green synthesis method provides higher stability, enhanced thermal properties, and a high surface area through the available phytochemicals in the Rhus coriaria L. extract.

1. Introduction

Researchers have recently focused on nanotechnology due to the extraordinary growth and development in this field, with the expectation that it will improve the current standard of

Competing interests: The authors have declared that no competing interests exist.

living in society [1]. In addition, nanoparticles (NPs) have attracted the interest of researchers worldwide owing to their unique qualities, including shape, size, and distribution, which can be utilized in many applications [2]. In recent times, silica (SiO_2) NPs are widely paid great attention in several applications as a result of their simplicity, stability, low toxicity, superior biocompatibility, and the ability to be functionalized with a variety of polymers and molecules, in addition to controllable particle sizes [3, 4]. The development of the SiO_2 NPs in different applications, such as technology, building industry, agriculture, food industry, medical and consumer products, have a great impact on altering and improving the industries [5]. In addition, SiO_2 NPs have been intensively used in the foundation of the advanced building industry, especially in concrete and cement-based materials, to increase compressive strength, the main goal of civil engineers, and thus reduce cement consumption greenhouse gas emissions [6]. Two distinct reaction processes can occur during the hydration of cement in the presence of nano-silica [7]. When nano-silica is applied to cement, H_2SiO_2 particles will be formed and engage with the existing Ca^{2+} to generate additional calcium-silicate-hydrate particles (C-S-H). Such particles are distributed in the water among the cement grains and perform as seeds to generate a much more compacted C-S-H phase [8]. The C-S-H phase production is no longer restricted to the grain surface alone but also occurs in the pore space [9]. As a result of the production of a high number of seeds, early cement hydration is accelerated [10]. Fig 1 shows, apart from the effective factor on the size and shape of SiO_2 NPs, the uniformity of dispersion and separation of particles, i.e., dis-agglomeration. These are important features and significantly affect the above-mentioned chemical reactions.

In general, as shown in Fig 2, three distinct strategies are available for the synthesis of NPs: chemical, physical, and biological [11]. The physical techniques require highly sophisticated machines with high pressure and high temperatures, some of which are complicated and costly [12]. Chemical procedures negatively impact the employment of chemical materials as reducing agents, which raises many worries regarding employees and the environment [13].

Recently, biological methods or green processes have been introduced as a novel method for synthesizing NPs vital, easy, and economical [14]. This method is a safe and environmentally friendly method for nanomaterial production, which is considered an alternative to conventional physical and chemical techniques [15]. This method has opened a new gate in front of the researchers to produce metal, metal oxide, and semiconductor NPs in a one-pot method. In fact, green synthesis methods of NPs using plant extraction, fungi, algae, and microbes have numerous advantages, especially for biomedical applications [16]. Among all green methods, plants have noteworthy quantities due to a huge number of phytochemicals such as flavonoids, polyphenols, glycosides, terpenoids, and proteins [17]. The most significant difference between green synthesis and other techniques for producing NPs is that, first, the NPs are reduced, capped, and stabilized by the phytochemicals present in the plant extractions [18, 19]. Second, these phytochemicals are antioxidants, ecologically friendly, and can be obtained easily from plant extracts [20]. Third, after NP preparation, some residual functional groups are tied with the NPs and cap the NPs. This makes the NPs more responsive than the synthesized NPs by the other methods [21]. According to the chemical approach, it is not ecologically friendly. A number of the reducing agents are harmful, which means that they have destructive effects on human life and the environment and are prohibitively expensive [22, 23]. Table 1 summarizes the approach for green synthesis of SiO_2 NPs as provided by researchers. Except for the last one, they used green synthesis in the first stage to produce sodium silicate (Na_2SiO_3), and chemical synthesis in the second (final) stage to produce SiO_2 NPs. The novelty of this study is that it used green synthesis to manufacture SiO_2 NPs from their first product (Na_2SiO_3), completing their approach entirely using green synthesis. This investigation is our ongoing study in the green synthesis NPs area [24–35].

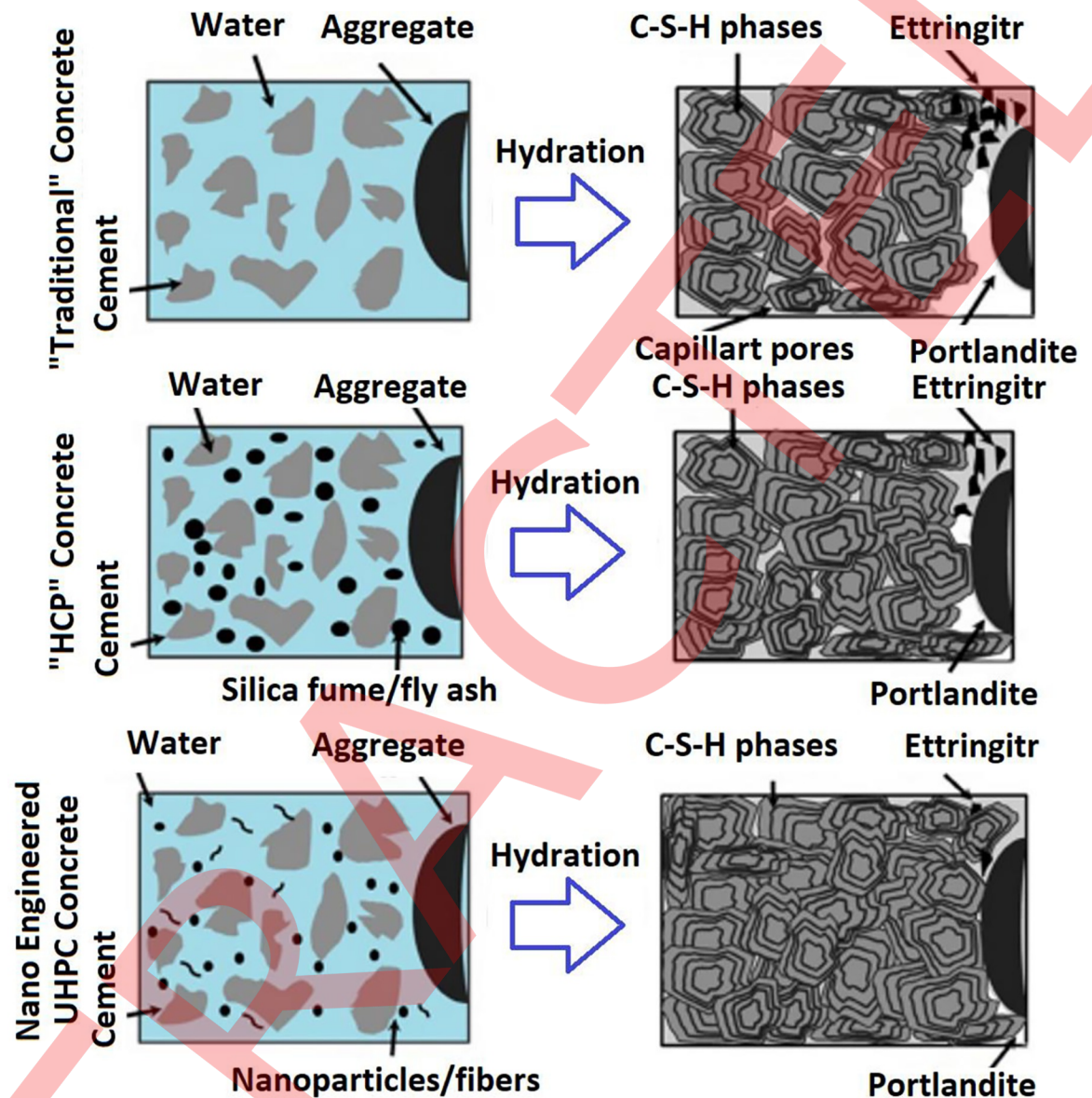


Fig 1. Traditional, high performance and nano-enhanced UHPC concrete.

<https://doi.org/10.1371/journal.pone.0268184.g001>

In this study, a certain amount of nano-silica was produced by the green method using *Rhus coriaria* L. extract. At the same time, a certain amount of nano-silica was chemically synthesized using Sol-gel method [44]. For both samples, numerous characterization techniques, including Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), Zeta potential, field emission scanning electron microscopy (FESEM), Transmission Electron Microscope analysis (TEM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) analysis, and dynamic light scattering (DLS) were utilized. Consequently, it was found that the green synthesized silica NPs, in general, possess superior properties over the chemically synthesized silica NPs.

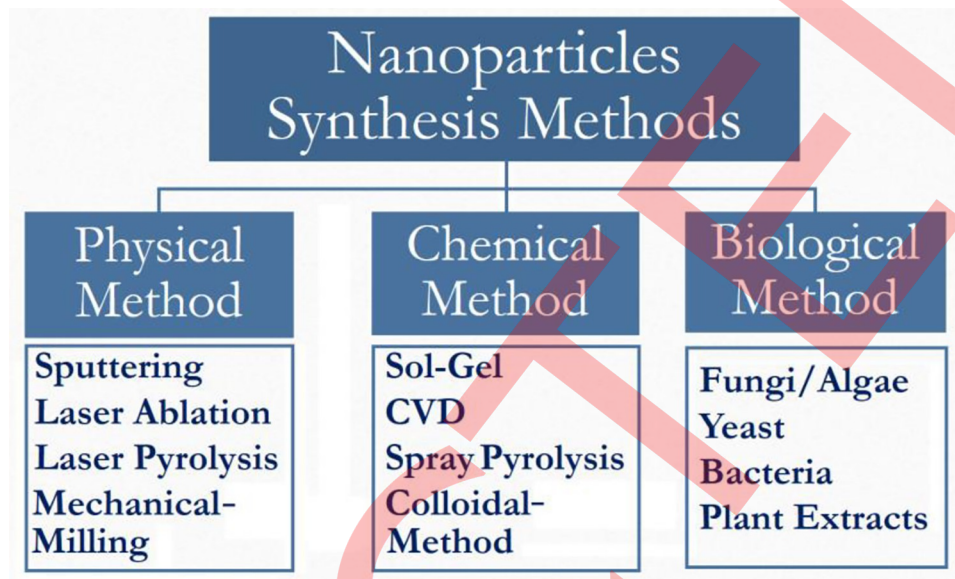


Fig 2. Nanoparticles can be synthesized through physical, chemical, and biological processes.

<https://doi.org/10.1371/journal.pone.0268184.g002>

2. Experimental procedure

2.1. Materials and methods

Sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) Molecular weight 212.14 g/mol, and purity >98.8 per-cent was used for synthesizing nanosilica using the green synthesis method. Sodium hydroxide (NaOH) with a Molecular weight of 40 g/mol was used to control the pH value of the growth solution. A sealed bottle of commercial nanosilica with 99% purity has been used in this study for comparison. All these materials and salts were ordered from Sigma-Aldrich Company. In addition, *Rhus coriaria* L. seeds were provided from Akre city, located in the Dohuk Governor-ate in the Kurdistan Region of Iraq. The latitude and longitude coordinates of Akre city are 36.741390 and 43.893333. The hot plate temperature was set at 80°C during the SiO_2 nanopar-ticles synthesis. The chemically synthesized SiO_2 NPs were prepared using Verma and Bhatta-charya's procedure [44].

Table 1. Production nanosilica using green synthesis in literature.

Primary stage					Final stage						
Green SiO ₂ source		Chemical reactant	Primary product		Chemical reactant	plant extract		Final product			Ref
Plant species	Part					Plant species	Part	NPs	Size (nm)	Shape	
Bamboo	Leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	various	Spherical	[36]
Bamboo	Leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	70–90	Spherical	[37]
Olive	Leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	30–40	Spherical	[38]
Sugarcane	Leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	29.13	Hexagonal	[39]
Rice	Leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	39.47	Spherical	[39]
Weed	Leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	30.56	Spherical	[39]
Sugarcane bagasse	Stem, leaf	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	30	Spherical	[40]
Rice	Husk	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	various	Spherical	[41]
Pine	Cone	NaOH	Na ₂ SiO ₃	+	H ₂ SO ₄	-	-	Silica	20	Spherical	[42]
-	-	-	-		SiC ₈ H ₂₀ O ₄	coconut	coir pith	Silica	18	Spherical	[43]

<https://doi.org/10.1371/journal.pone.0268184.t001>

2.2. Characterization

To study the structure of SiO₂ nanoparticles, X-ray diffraction (XRD) machine was utilized by using PANalytical (Cu_K = 1.54 nm). The scanning value was 1° per minute in the scope of 10° up to 80°. To confirm the formation of SiO₂ NPs, the UV-Vis technique was performed using a double beam spectrophotometer (Super Aquarius Spectrophotometer-1000). Field emission scanning electron microscopy (FESEM Quanta 450) was used to study the morphology and grain dispersion. The elemental composition of the produced nanostructures was determined using dispersive X-ray spectroscopy (EDX), installed inside FESEM. The functional groups from leaf extracts attached to the SiO₂ NPs were studied by attached to the SiO₂ NPs using a Fourier transform infrared (Perkin Elmer FTIR) spectrophotometer in the acquisition range of 400–4000 cm⁻¹. Dynamic light scattering was used to determine the size of SiO₂ NPs. The DSC curve was performed using a differential scanning calorimetry (DSC) type (TA Instruments USA, DSC Q10) in the temperature range of 50–600°C. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer-Pyris1 analyzer (USA).

2.3. Preparing of *Rhus coriaria* L. extract

Rhus coriaria L. seeds were collected and dried in a shadow area at 25°C, then crushed using a grinder machine. Then, 50 g of crushed *Rhus coriaria* L. was heated by magnetic stirring in 100 ml of double-distilled water for 40 minutes. The final mixture was filtered through the filter paper, and the pure extract was stored in the refrigerator for further use.

2.4. Silica nanoparticles (SiO₂ NPs) synthesis using the green method

20 mL Na₂SiO₃ was added dropwise to 100 mL of freshly generated *Rhus coriaria* L. extract while the mixture was being stirred at 60°C. The procedure was carried out under reflux conditions for 12 hours at pH 9 until the SiO₂ NPs were synthesized. The pH value of the solution was adjusted using 0.1 M NaOH, which was dissolved well in 50 mL of double-distilled water. Therefore, the mixture was filtered, and the obtained precipitate was washed carefully with double distilled water three times and methanol to remove all contamination. Centrifugation at 7000 rpm for 25 minutes separated the residues from the mixture, then heated at 550°C for 45 minutes in a furnace to eliminate any contaminants and organic elements around the SiO₂ NPs. Then as indicated in Fig 3, the residue was dried in an oven and kept for further characterization and application activities.

3. Results and discussion

3.1. Characterization of green synthesized (GS) and chemically synthesized (CS) SiO₂ NPs

The morphology, structure, optical, toughness, and thermal properties of both types of SiO₂ NPs have been investigated using several characterization techniques.

3.1.1. FTIR Spectroscopy. Infrared spectroscopy has been extensively used to identify the functional group's modification and bonding properties of nanomaterials. The FTIR spectrum analysis might give valuable information about the structure, chemical composition, and purity of NPs. It can also identify and classify probable biomolecules that can be reliable for capping, leading to proficient stabilization of the NPs. The samples containing the NPs are entirely dried and ground with KBr pellets and investigated. Scanning is confirmed to acquire a covered signal-to-noise ratio for suitable consequences. Fig 4 illustrates a typical FTIR spectrum of colloidal silica nanoparticles reported for both GS-SiO₂ NPs and CS-SiO₂ NPs. According to Fig 4A, two dominant peaks were observed at around 1053 cm⁻¹ and 786 cm⁻¹,

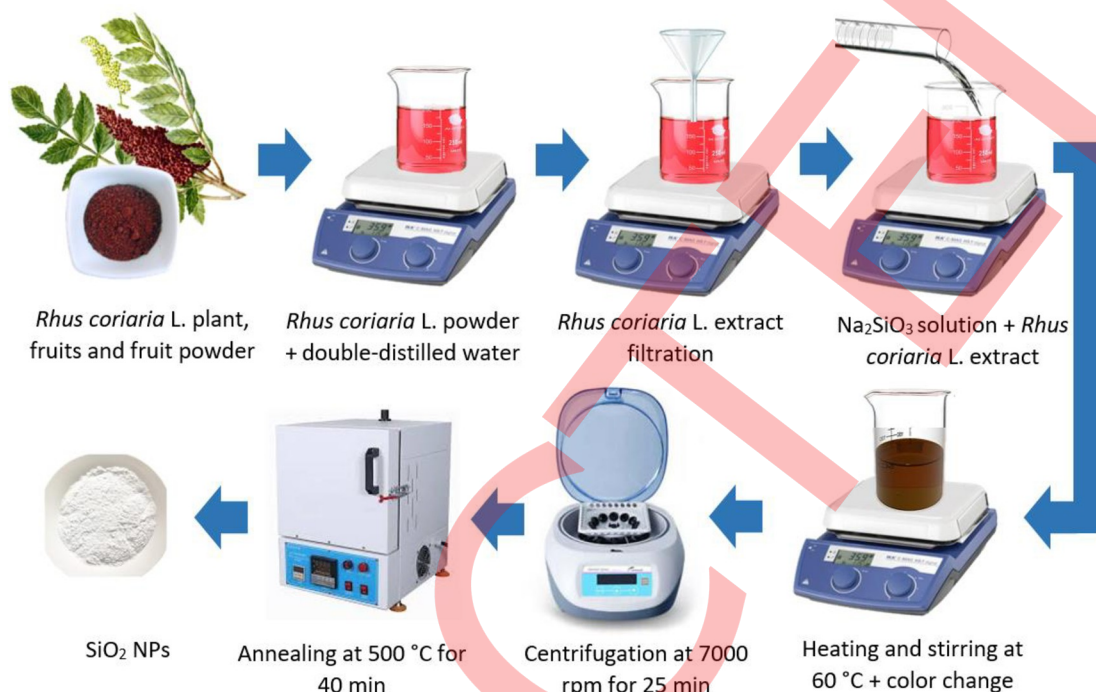


Fig 3. Schematic diagram of the green synthesis process of SiO₂ NPs using *Rhus coriaria* L. extract.

<https://doi.org/10.1371/journal.pone.0268184.g003>

which are related to the asymmetric stretching vibration of the siloxane bond (Si-O-Si) and the symmetrical vibration of the Si-O bond [4, 45]. While from Fig 4B, it is clear that the bands nearby 3468 cm⁻¹ is associated with the Si-OH, which is usually characteristic of the OH group corresponding to the available phytochemical in *Rhus coriaria* L. extract [37]. In addition, the band at 1637 cm⁻¹ is caused by the scissor bending vibration of water molecular H₂O. Similarly, the peaks at 1097 and 802 cm⁻¹ correspond to the asymmetric stretching of the Si-O-Si and Si-O band bending vibrations, respectively. Moreover, the band at 463 cm⁻¹ was connected with the bending vibration of O-Si-O modes [46].

3.1.2. X-ray diffraction. To study the crystalline structure of both chemical approach and green synthesized of SiO₂ NPs, the X-ray diffraction (XRD) analysis was carried out as shown

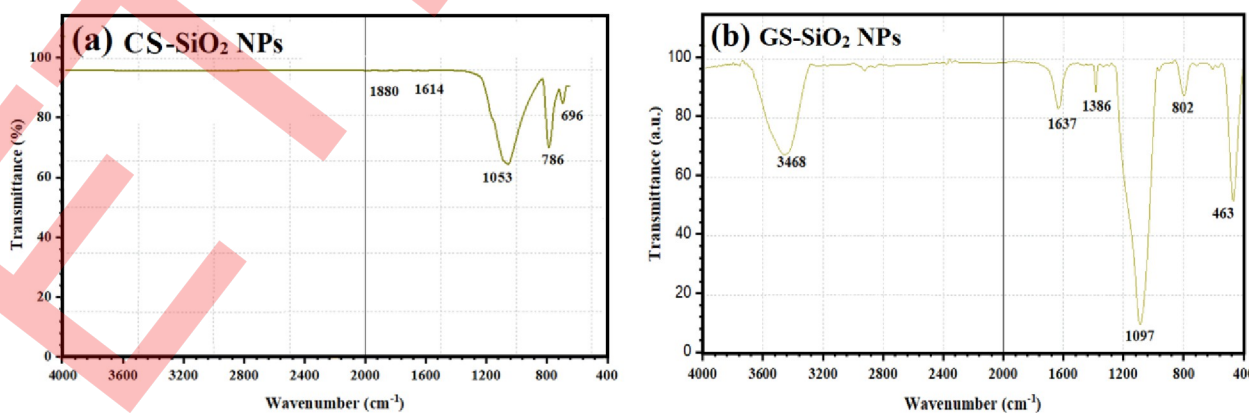


Fig 4. FTIR spectra of (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g004>

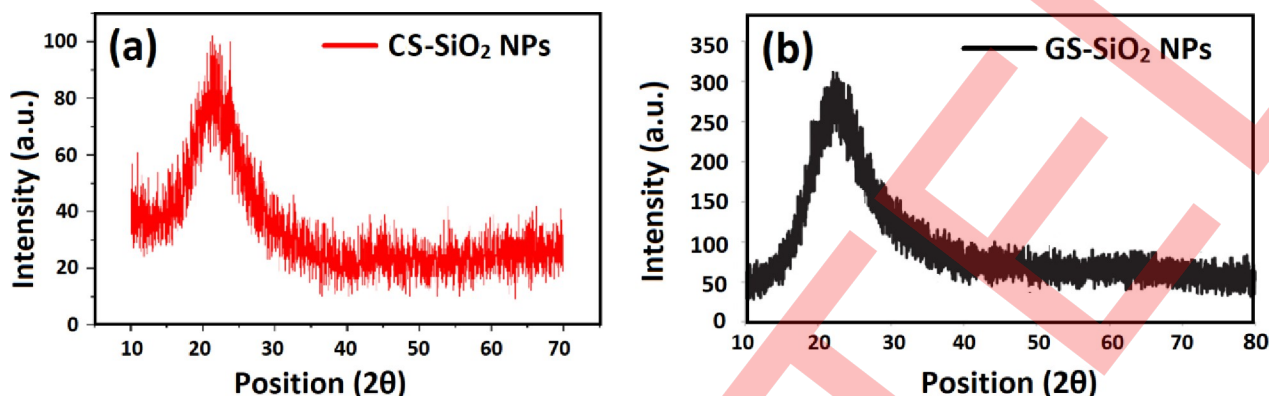


Fig 5. X-ray diffraction spectra of (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g005>

in Fig 5. For both, the commercial SiO₂ NPs (Fig 5A) and the green synthesized SiO₂ NPs (Fig 5B), a broad peak centered at $2\theta = 23^\circ$ ($hkl = 100$) is observed, which can be assigned to the SiO₂ NPs and no other diffraction peaks can be detected [4]. Fig 5 illustrates this point. That the X-ray diffractograms in both instances confirmed the amorphous nature of the SiO₂ NPs [47]. Also, in both cases, the wide peaks display a whole amorphous structure. Nevertheless, the green synthesized SiO₂ NPs show relatively lower noise than the chemically synthesized SiO₂ NPs. It can be stated that the peaks were matched with the reference JCPDS file No. 89–0510 for SiO₂, and it discloses no impurities peak for SiO₂ [48].

The particle size (D) of the CS-SiO₂ NPs and GS-SiO₂ NPs was calculated using Debye-Scherrer equation [49].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the wavelength of the utilized X-ray ($\lambda = 1.5406 \text{ \AA}$), β is the full width at half maximum (FWHM) of the most intense peak, and θ is the Bragg's angle. From the previous equation, the SiO₂ NPs sizes were 18 nm and 23 nm for the CS-SiO₂ NPs and the GS-SiO₂ NPs, respectively. The absence of sharp peaks shows that there is no crystalline structure of the SiO₂ NPs. The GS-SiO₂ NPs produced by *Rhus coriaria* L. extract is an outstanding process, and the yield is close to 100 percent. This is a very encouraging result, and it was expected since plant extracts were utilized instead of the toxic chemical. Also, the phytochemicals present in the plant extracts acted as a reduction, capping, and stabilizing agent of the GS-SiO₂ NPs.

3.1.3. FESEM analysis. The surface morphology of the CS-SiO₂ NPs and the GS-SiO₂ NPs was primarily determined by FESEM, and the results are shown in Fig 6. It can be seen that the majority of the SiO₂ NPs in both samples are on the nanoscale and possess a spherical shape. The main difference between the CS-SiO₂ NPs and the GS-SiO₂ NPs is that the green synthesized method produces polydisperse NPs, while in the chemically synthesized sample, most of the NPs are monodisperse NPs with different particle sizes. The formation of tiny particles as a result of a rise in the concentration of the OH group causes a decrease in the rate of condensation and hydrolysis process, which in turn inhibits the formation of bigger particles. Furthermore, the SiO₂ nanoparticles are somewhat agglomerated, which is characteristic of the green synthesis method. This is attributed to the fact that nanoparticles have a larger surface area and long-lasting affinity throughout the dehydrating process, which causes agglomeration of the particles [22, 23]. It can be noted that the phytochemicals inside plant extraction

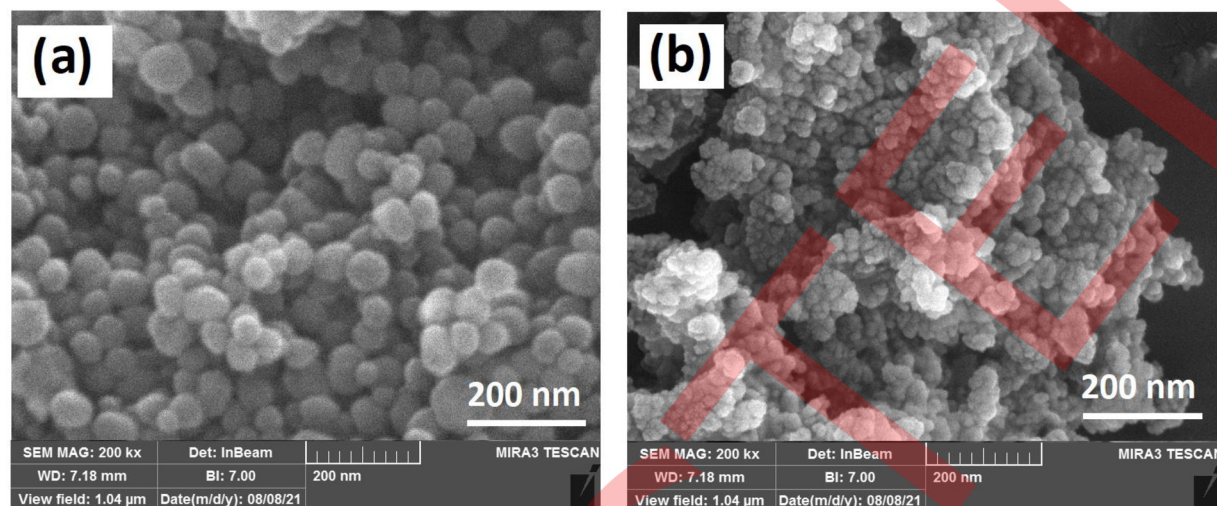


Fig 6. FESEM images of (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g006>

have a significant effect on the stability of NPs and their agglomeration. As a result, the SiO₂ NPs adhere to one another and spontaneously produce asymmetrical clusters [24, 26]. The process for fabricating the SiO₂ NPs is related to a number of growth factors, including the growth time, the concentration of plant extract, the pH value of the solution, the temperature of the solution, and the concentration of salt. Consequently, calibration of these growth components is critical to accomplishing the desired shape and size of nanoparticles to allow for their maximal modification and request.

3.1.4. Transmission Electron Microscope (TEM) analysis. Fig 7 displays the TEM analysis of the obtained CS-SiO₂ NPs and the GS-SiO₂ NPs. The outcomes confirmed that the SiO₂ NPs possess a spherical shape in both cases. The average size of the CS-SiO₂ NPs is around 30 nm, while the average size of the GS-SiO₂ NPs is around 55 nm and the NPs were amorphous in nature. It can be stated that only TEM and DLS analysis provide the real size of the

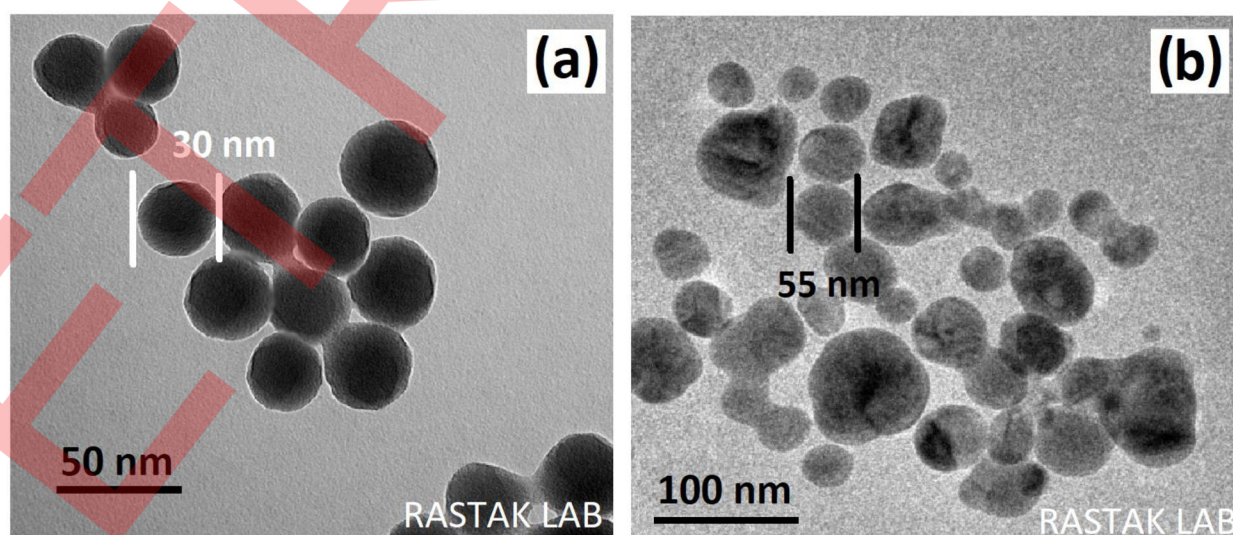


Fig 7. TEM images of (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g007>

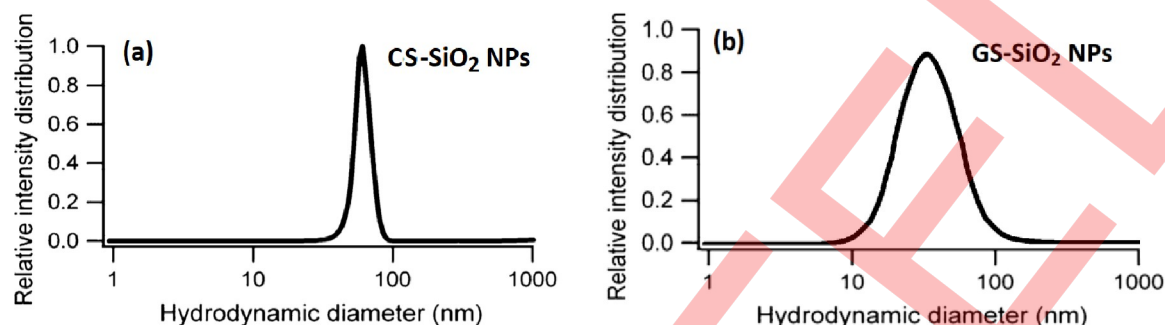


Fig 8. DLS for (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g008>

synthesized NPs. This outcome agrees in high precision with the DLS results discussed in the next section. The results of this study agree with the results obtained by Yadav and Fulekar [50].

3.1.5. Dynamic light scattering (DLS). DLS is used to calculate the consistent size of the SiO₂ NPs distributed in the water medium. The size distribution profile of the chemically and green synthesized SiO₂ NPs using the DLS technique is shown in Fig 8. This study found that the average diameter for chemically and green synthesized SiO₂ NPs was 32 nm and 60 nm. DLS measurements (Fig 8) showed that the hydrodynamic diameter of the SiO₂ NPs stayed nearly unchanged during the measurement for one hour. The green synthesis method generally provides smaller NPs than the chemical methods [46].

Additionally, the CS-SiO₂ NPs remained monodisperse throughout the DLS test. The statement that some engineered NPs, such as SiO₂, tend to combine and agglomerate speedily to form bigger particles, with sizes beyond the nanoscale, might bring together an extra level of difficulty to describe particle performance in the aqueous medium [51]. Nevertheless, this larger agglomeration will normally resolve swiftly by using an ultrasonic bath. Several researchers have achieved comparable results [52].

3.1.6. Zeta potential. Zeta potential is one of the most significant factors that explain the rheological performance of ceramic suspensions. The zeta potential is a measurement of the real electric field around the surface of the nanoparticle [53]. When a nanoparticle is charged totally, the amount of the charge is calculated by the ion concentration versus different charges close to the surface of the NPs. The greater the level of zeta potential, the stronger the surface repulsion/attraction. For the determination of the Zeta potential, it is necessary to consider the mobility of nanoparticles under the influence of an applied electromagnetic field. This work demonstrated that the capping molecules present on the surface of the green produced SiO₂ NPs are mostly made of negative charge families and that they are also accountable for the stability of the NPs in the growing solution, as shown before [54].

The Zeta potential gives information about the stability of the particles. Fig 9 shows the zeta potential analysis for both the CS-SiO₂ NPs and the GS-SiO₂ NPs. It can be regarded that the values of zeta potential for CS-SiO₂ NPs and the GS-SiO₂ NPs are -38 mV and -45 mV, respectively. This is a good indicator that GS-SiO₂ NPs provide stable NPs. The variation of the zeta potential value between the CS-SiO₂ NPs and the GS-SiO₂ NPs is most likely due to the agglomeration that has been shown in the SEM analysis. To a great extent, agglomeration is associated with the green synthesis method. This is more likely due to the insufficient number of capping agents around the NPs in some plant extracts [55]. Conventional methods for synthesizing NPs involve high-priced chemical and physical procedures that frequently utilize hazardous ingredients, most of which are carcinogenic. These issues arise mostly from utilizing organic

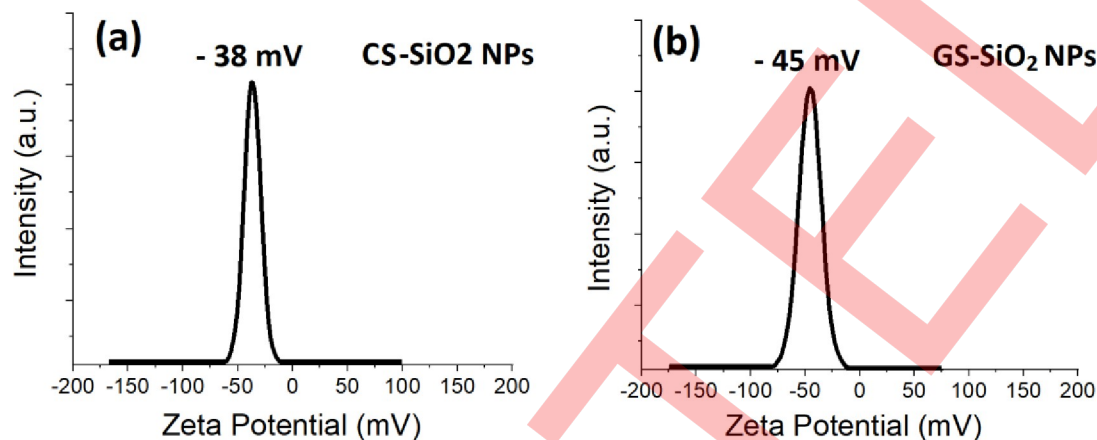


Fig 9. Zeta potential for (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g009>

solvents that work as reducing, capping, and stabilizing agents that prevent the NPs from agglomerating. Consequently, the presence of these toxic creation agents during the synthesizing process limits the application of the NPs in environmental and biomedical applications [56]. Accordingly at present, researchers are focusing on a harmless, consistent, inexpensive, and environmentally-friendly method to prepare NPs.

3.1.7. Differential scanning calorimetry (DSC) analysis. The morphology analysis of the SEM images shows that the GS-SiO₂ NPs possess agglomeration. More importantly, the agglomeration can be affected by the temperature. Thus, the thermal behavior of SiO₂ NPs is investigated by DSC analysis at temperatures varying from 25 to 1000°C as shown in Fig 10. The slow heating rate of 10°C/min was chosen to observe similar behavior for both chemically and green-synthesized SiO₂ NPs. From Fig 10, it can be regarded that the DSC curve of CS-SiO₂ NPs clearly shows one endothermic peak, centered at 115°C, and one exothermic peak, centered at 537°C. While the DSC curve of GS-SiO₂ NPs shows one endothermic peak, centered at 190°C, and two exothermic peaks, centered at 55°C and 522°C, respectively. The endothermic peak temperatures of 115°C and 190°C, which were began at 100°C, for both the CS-SiO₂ and the GS-SiO₂ NPs may be due to dehydration, which is the simultaneous removal

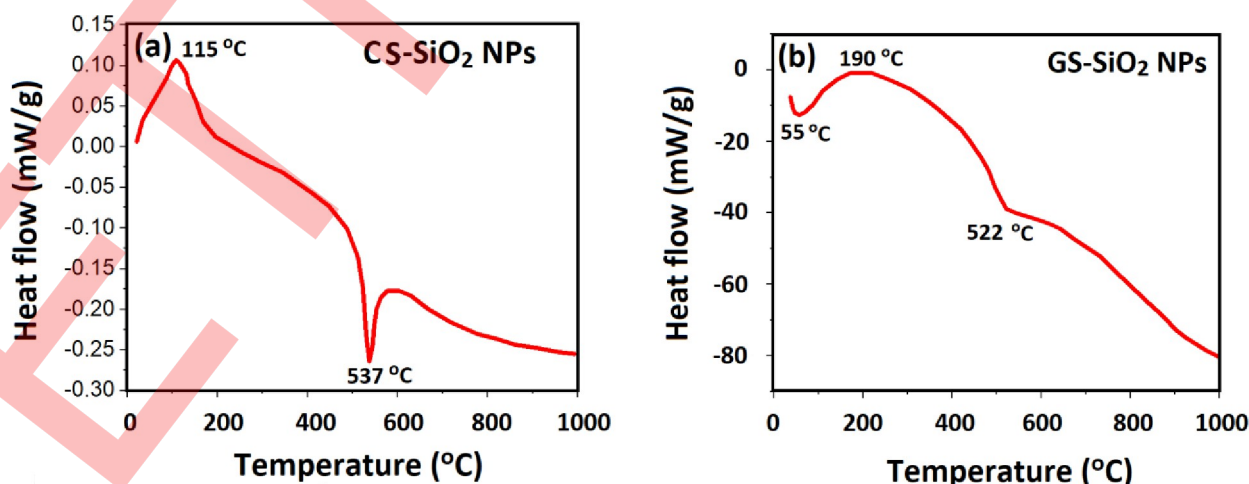


Fig 10. DSC analysis for (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g010>

of physisorbed surface moisture of SiO₂ NPs. This is a very good indicator that the GS-SiO₂ NPs are stronger absorbers of the surrounding moisture. This obvious endothermic peak shift is more likely due to the dihydroxylation due to the hydroxyl groups (OH) condensation in GS-SiO₂ NPs. Kim et al. [57] stated that the right reduction of SiO₂ NPs occurs at temperatures ranging from 150°C to 550°C. As a result, it can be decided that this substantial weight reduction is related to removing water and the decomposition of some of the functionalizing agents [58]. This decomposition, accompanied by an exothermic peak, occurs between 400 and 550°C. Similar results have been found by other authors [59], stating that above 600°C, the inaccessible hydroxyl groups are gradually eliminated, resulting in a little mass loss. Another significant trend in the DSC curve is that the GS-SiO₂ NPs possess more heat capacity than the CS-SiO₂ NPs. This can be reflected directly on the heat flow rate in both cases. Again, this is an excellent indicator that the GS-SiO₂ NPs are better than the CS-SiO₂ NPs, especially in solar cells, electronic devices, and engineering applications [60].

3.1.8. Thermogravimetric analysis (TGA). DSC and TGA are two of the most extensively utilized thermal analysis techniques in the characterization of crystalline and amorphous materials. However, TGA is a complementary technique to DSC analysis. Briefly, the TGA technique monitors the weight of the sample during the heating or cooling process. However, DSC determines the amount of energy absorbed or released by a sample throughout the cooling or heating procedure. The thermal stability of both CS-SiO₂ and GS-SiO₂ NPs as a function of temperature has been investigated using the TGA technique. Fig 11 shows the TGA state of both CS-SiO₂ and GS-SiO₂ NPs. Through comparing their TGA curves, it can be seen that the GS-SiO₂ NPs are more thermally stable than the CS-SiO₂ NPs. It loses only 7% of its weight at ~400°C. The CS-SiO₂ NPs lose ~90% of their weight at this temperature. This is no surprise since the DSC analysis reinforces these consequences. This remarkable weight loss in the CS-SiO₂ NPs could be attributed to the decomposition of the attached organic groups [61]. On the other hand, Fig 11 indicates that both CS-SiO₂ and GS-SiO₂ NPs lose about 4% of their weight due to water molecules' evaporation. The significant weight loss occurred between 200–450°C, and 200–750°C for CS-SiO₂ and GS-SiO₂ NPs, respectively. Again, this is a very good indicator that the capping and stabilizing agents around the GS-SiO₂ NPs are strong enough to resist high temperatures [62]. While the major weight loss for CS-SiO₂ NPs occurs

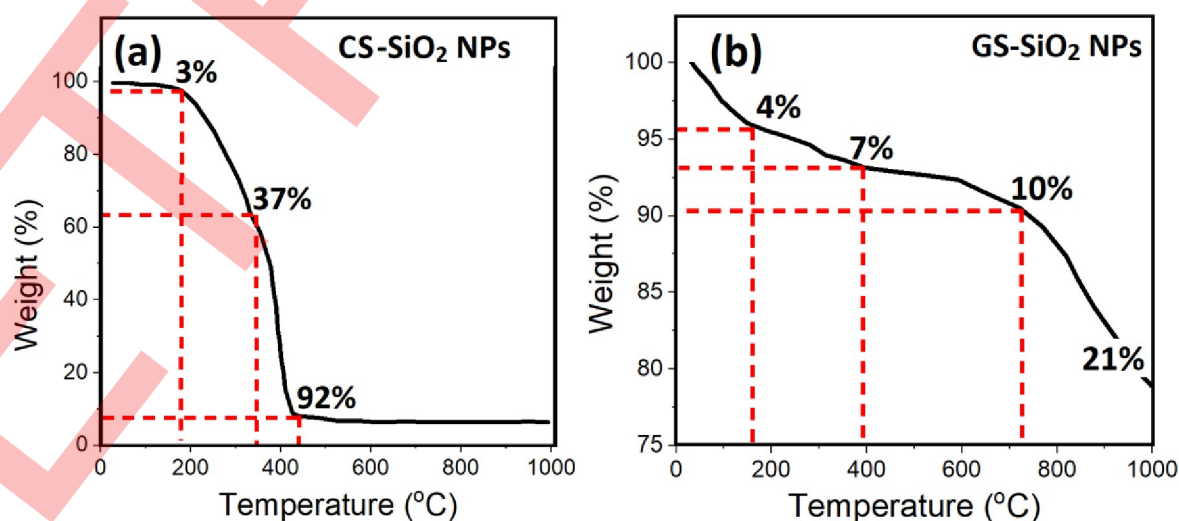


Fig 11. TGA analysis for (a) CS-SiO₂ NPs and (b) GS-SiO₂ NPs.

<https://doi.org/10.1371/journal.pone.0268184.g011>

at a temperature $\sim 400^{\circ}\text{C}$, which is $\sim 92\%$. Consequently, this study showed that GS-SiO₂ NPs could be utilized in high-temperature devices and applications [60].

4. Conclusions

This study demonstrated that spherical, nano-sized, thermally stable SiO₂ NPs could be synthesized using a green method. This method is eco-friendly, one-pot, cheap, productive, and leads traditional synthesizing methods. Rhus coriaria extract, as a reducing, capping, and stabilizing agent, used with sodium metasilicate (Na₂SiO₃·5H₂O), as a precursor, under reflux conditions and pH 9. Several The shape, purity, crystal structure, stability, thermal, and optical characteristics of biosynthesized SiO₂ were investigated using characterization methods. Considering all of these aspects, the green synthesized SiO₂ NPs were compared with the chemically synthesized SiO₂ NPs.

1. FTIR analysis for CS-SiO₂ NPs demonstrated two dominant peaks at roughly 1053 cm⁻¹ and 786 cm⁻¹, which are associated with the asymmetric stretching vibration of the Si-O bond. While FTIR for GS-SiO₂ NPs revealed that the peak at 3468 cm⁻¹ is related to the Si-OH, the peak at 3468 cm⁻¹ is related to the Si-OH, which normally characteristics of the OH group match the accessible phytochemical in Rhus coriaria.
2. According to the XRD measurements, both GS and CS SiO₂ NPs had the same peaks at $2\theta = 23^{\circ}$, which confirmed the JCDPS reference. Although the intensity of the GS-SiO₂ NPs was higher than the CS-SiO₂ NPs, this was due to phytochemical presence in green synthesis.
3. The morphological studies revealed that the CS-SiO₂ NPs possess monodisperse NPs while the GS-SiO₂ NPs show polydisperse NPs. This is more likely due to the fact that in the green synthesis method, different phytochemicals are participating in reducing capping and stabilizing the process. Besides, the FESEM images revealed that CS and GS SiO₂ NPs are spherical in shape with a minimum degree of agglomeration, and the NP sizes were between 45~60 nm and 10~15 nm, respectively.
4. The effect of this agglomeration on the zeta potential analysis was not shown. In other words, although the particles are agglomerated, GS-SiO₂ NPs provide good NPs stability.
5. The DSC analysis of CS-SiO₂ NPs displays that there is one endothermic peak, centered at 115°C and one exothermic peak, centered at 537°C. Whereas the DSC analysis of GS-SiO₂ NPs shows one endothermic peak, centered at 190°C and two exothermic peaks, centered at 55°C and 522°C, respectively.
6. The TGA analysis shows that the GS-SiO₂ NPs are more thermally stable than the CS-SiO₂ NPs. It loses only 7% of its weight at $\sim 400^{\circ}\text{C}$. The CS-SiO₂ NPs lose 90% of their weight at this temperature. The overall results revealed that the green synthesis of SiO₂ nanoparticles was better than chemically synthesized SiO₂ in terms of particle stability and thermal properties.

Acknowledgments

The authors like to express their gratitude to Dr. Mukhtar Ahmed of SISAF at Ulster University in the United Kingdom for his invaluable support during this inquiry. Additionally, they like to express their gratitude to Dr. David M.W. Waswa of Tishk International University for his meticulous editing of this work.

Author Contributions

Conceptualization: Chiya Yousef Rahimzadeh, Azeez Abdullah Barzinjy, Samir Mustafa Hamad.

Data curation: Chiya Yousef Rahimzadeh, Samir Mustafa Hamad.

Formal analysis: Chiya Yousef Rahimzadeh, Ahmed Salih Mohammed, Samir Mustafa Hamad.

Funding acquisition: Chiya Yousef Rahimzadeh, Ahmed Salih Mohammed, Samir Mustafa Hamad.

Investigation: Azeez Abdullah Barzinjy.

Methodology: Azeez Abdullah Barzinjy.

Project administration: Azeez Abdullah Barzinjy.

Resources: Azeez Abdullah Barzinjy.

Validation: Samir Mustafa Hamad.

Visualization: Samir Mustafa Hamad.

Writing – original draft: Samir Mustafa Hamad.

Writing – review & editing: Samir Mustafa Hamad.

References

1. Stark W.J., et al., Industrial applications of nanoparticles. *Chemical Society Reviews*, 2015. 44(16): p. 5793–5805. <https://doi.org/10.1039/c4cs00362d> PMID: 25669838
2. Pitkethy M.J., Nanoparticles as building blocks? *Materials Today*, 2003. 6(12): p. 36–42.
3. Bahmani S.H., et al., Stabilization of residual soil using SiO₂ nanoparticles and cement. *Construction and Building Materials*, 2014. 64: p. 350–359.
4. Dubey R., Rajesh Y., and More M., Synthesis and characterization of SiO₂ nanoparticles via sol-gel method for industrial applications. *Materials Today: Proceedings*, 2015. 2(4–5): p. 3575–3579.
5. Niksefat N., Jahanshahi M., and Rahimpour A., The effect of SiO₂ nanoparticles on morphology and performance of thin film composite membranes for forward osmosis application. *Desalination*, 2014. 343: p. 140–146.
6. Dyshlyuk L., et al., Antimicrobial potential of ZnO, TiO₂ and SiO₂ nanoparticles in protecting building materials from biodegradation. *International Biodeterioration & Biodegradation*, 2020. 146: p. 104821.
7. Rai S. and Tiwari S., Nano silica in cement hydration. *Materials Today: Proceedings*, 2018. 5(3): p. 9196–9202.
8. Kong D., et al., Whether do nano-particles act as nucleation sites for CSH gel growth during cement hydration? *Cement and Concrete Composites*, 2018. 87: p. 98–109.
9. Land G. and Stephan D., The effect of synthesis conditions on the efficiency of CSH seeds to accelerate cement hydration. *Cement and Concrete Composites*, 2018. 87: p. 73–78.
10. Aleem S.A.E., Heikal M., and Morsi W., Hydration characteristic, thermal expansion and microstructure of cement containing nano-silica. *Construction and Building Materials*, 2014. 59: p. 151–160.
11. Iravani S., et al., Synthesis of silver nanoparticles: chemical, physical and biological methods. *Research in pharmaceutical sciences*, 2014. 9(6): p. 385. PMID: 26339255
12. Rajput N., Methods of preparation of nanoparticles-a review. *International Journal of Advances in Engineering & Technology*, 2015. 7(6): p. 1806.
13. Hyeon T., Chemical synthesis of magnetic nanoparticles. *Chemical communications*, 2003(8): p. 927–934. <https://doi.org/10.1039/b207789b> PMID: 12744306
14. Nadaroglu H., GÜNGÖR A.A., and Selvi İ., Synthesis of nanoparticles by green synthesis method. *International Journal of Innovative Research and Reviews*, 2017. 1(1): p. 6–9.
15. Parveen K., Banse V., and Ledwani L. Green synthesis of nanoparticles: their advantages and disadvantages. in *AIP conference proceedings*. 2016. AIP Publishing LLC.

16. Chandra H., et al., Medicinal plants: Treasure trove for green synthesis of metallic nanoparticles and their biomedical applications. *Biocatalysis and Agricultural Biotechnology*, 2020. 24: p. 101518.
17. Jadoun S., et al., Green synthesis of nanoparticles using plant extracts: A review. *Environmental Chemistry Letters*, 2021. 19(1): p. 355–374.
18. Ahmed A.A., et al., Neodymium oxide nanoparticles synthesis using phytochemicals of leaf extracts of different plants as reducing and capping agents: Growth mechanism, optical, structural and catalytic properties. *Journal of the Chinese Chemical Society*. n/a(n/a).
19. Mubeen I. and Farrukh M.A., Mechanisms of green synthesis of iron nanoparticles using *Trifolium alexandrinum* extract and degradation of methylene blue. *Inorganic and Nano-Metal Chemistry*, 2021: p. 1–10.
20. Kumar H., et al., Fruit extract mediated green synthesis of metallic nanoparticles: A new avenue in pomology applications. *International journal of molecular sciences*, 2020. 21(22): p. 8458. <https://doi.org/10.3390/ijms21228458> PMID: 33187086
21. Iravani S., Green synthesis of metal nanoparticles using plants. *Green Chemistry*, 2011. 13(10): p. 2638–2650.
22. Tso C.-p., et al., Stability of metal oxide nanoparticles in aqueous solutions. *Water science and technology*, 2010. 61(1): p. 127–133. <https://doi.org/10.2166/wst.2010.787> PMID: 20057098
23. Gour A. and Jain N.K., Advances in green synthesis of nanoparticles. *Artificial cells, nanomedicine, and biotechnology*, 2019. 47(1): p. 844–851.
24. A Barzinjy A., Characterization of ZnO Nanoparticles Prepared from Green Synthesis Using *Euphorbia Petiolata* Leaves. *Eurasian Journal of Science & Engineering*, 2019. 4(3): p. 74–83.
25. A Barzinjy A., Ionic liquids: Sustainable media for nanoparticles. *Jordan Journal of Physics*, 2019. 12(1): p. 45–62.
26. A Barzinjy A., Structure, synthesis and applications of ZnO nanoparticles: A review. *Jordan Journal of Physics*, 2020. 13(2): p. 123–135.
27. Azeza H.H. and Barzinjya A.A., Biosynthesis zinc oxide nanoparticles using *Apium graveolens* L. leaf extract and its use in removing the organic pollutants in water. *Desalination Water Treat*, 2020. 190: p. 179–192.
28. Barzinjy A.A. and Azeez H.H., Green synthesis and characterization of zinc oxide nanoparticles using *Eucalyptus globulus* Labill. leaf extract and zinc nitrate hexahydrate salt. *SN Applied Sciences*, 2020. 2(5): p. 1–14.
29. Barzinjy A.A., et al., Biosynthesis, characterization and mechanism of formation of ZnO nanoparticles using *Petroselinum crispum* leaf extract. *Current Organic Synthesis*, 2020. 17(7): p. 558–566. <https://doi.org/10.2174/1570179417666200628140547> PMID: 32598261
30. Barzinjy A.A., et al., Green and eco-friendly synthesis of Nickel oxide nanoparticles and its photocatalytic activity for methyl orange degradation. *Journal of Materials Science: Materials in Electronics*, 2020. 31(14): p. 11303–11316.
31. Barzinjy A.A., et al., Biosynthesis and characterisation of zinc oxide nanoparticles from *Punica granatum* (pomegranate) juice extract and its application in thin films preparation by spin-coating method. *Micro & Nano Letters*, 2020. 15(6): p. 415–420.
32. Sajadi S.M., et al., Green synthesis of the Ag/Bentonite nanocomposite Using *Euphorbia larica* extract: a reusable catalyst for efficient reduction of nitro compounds and organic dyes. *ChemistrySelect*, 2018. 3(43): p. 12274–12280.
33. Shnawa B.H., et al., Scolicidal activity of biosynthesized zinc oxide nanoparticles by *Mentha longifolia* L. leaves against *Echinococcus granulosus* protoscolices. *Emergent Materials*, 2021: p. 1–11.
34. Talabani R.F., et al., Biosynthesis of Silver Nanoparticles and Their Applications in Harvesting Sunlight for Solar Thermal Generation. *Nanomaterials*, 2021. 11(9): p. 2421. <https://doi.org/10.3390/nano11092421> PMID: 34578737
35. Nasrollahzadeh M., et al., Biosynthesis of the palladium/sodium borosilicate nanocomposite using *Euphorbia milii* extract and evaluation of its catalytic activity in the reduction of chromium (VI), nitro compounds and organic dyes. *Materials Research Bulletin*, 2018. 102: p. 24–35.
36. Silviana S. and Bayu W.J. Silicon conversion from bamboo leaf silica by magnesiothermic reduction for development of Li-ion battery anode. in *Matec web of conferences*. 2018. EDP Sciences.
37. Sharma P., et al., A novel and facile green synthesis of SiO₂ nanoparticles for removal of toxic water pollutants. *Applied Nanoscience*, 2021: p. 1–13.
38. Rezaeian M., et al., Green synthesis of silica nanoparticles from olive residue and investigation of their anticancer potential. *Nanomedicine*, 2021. 16(18): p. 1581–1593. <https://doi.org/10.2217/nnm-2021-0040> PMID: 34169748

39. Sachan D., Ramesh A., and Das G., Green synthesis of silica nanoparticles from leaf biomass and its application to remove heavy metals from synthetic wastewater: A comparative analysis. *Environmental Nanotechnology, Monitoring & Management*, 2021. 16: p. 100467.
40. Mohd N.K., Wee N.N.A.N., and Azmi A.A. Green synthesis of silica nanoparticles using sugarcane bagasse. in *AIP conference proceedings*. 2017. AIP Publishing LLC.
41. Vijayalakshmi U., et al., Green synthesis of silica nanoparticles and its corrosion resistance behavior on mild steel. *J. Indian Chem. Soc.*, 2015. 92(5): p. 675–678.
42. Assefi M., Davar F., and Hadadzadeh H., Green synthesis of nanosilica by thermal decomposition of pine cones and pine needles. *Advanced powder technology*, 2015. 26(6): p. 1583–1589.
43. Maroušek J., et al., Silica Nanoparticles from Coir Pith Synthesized by Acidic Sol-Gel Method Improve Germination Economics. *Polymers*, 2022. 14(2): p. 266. <https://doi.org/10.3390/polym14020266> PMID: 35054673
44. Verma J. and Bhattacharya A., analysis on synthesis of silica nanoparticles and its effect on growth of *T. harzianum* & *Rhizoctonia* species. *Biomedical Journal of Scientific & Technical Research*, 2018. 10 (4): p. 7890–7897.
45. Jiang X., et al., Synthesis and formation mechanism of amorphous silica particles via sol–gel process with tetraethylorthosilicate. *Ceramics International*, 2019. 45(6): p. 7673–7680.
46. Abd-elmohsen S.A., et al., Green synthesis, Optimization and Characterization of SiO₂ nanoparticles using *Aspergillus tubingensis* F20 isolated from drinking water. *Novel Research in Microbiology Journal*, 2019. 3(6): p. 546–557.
47. Yu L.Y., Huang Z.X., and Shi M.X. Synthesis and characterization of silica by sol-gel method. in *Advanced Materials Research*. 2014. Trans Tech Publ.
48. Bajpai N., et al., Effects of rare earth ions (Tb, Ce, Eu, Dy) on the thermoluminescence characteristics of sol–gel derived and γ -irradiated SiO₂ nanoparticles. *Luminescence*, 2014. 29(6): p. 669–673. <https://doi.org/10.1002/bio.2604> PMID: 2422272
49. Holzwarth U. and Gibson N., The Scherrer equation versus the 'Debye-Scherrer equation'. *Nature nanotechnology*, 2011. 6(9): p. 534–534. <https://doi.org/10.1038/nnano.2011.145> PMID: 21873991
50. Yadav V.K. and Fulekar M., Green synthesis and characterization of amorphous silica nanoparticles from fly ash. *Materials Today: Proceedings*, 2019. 18: p. 4351–4359.
51. Yanagishita T., et al., Preparation of monodisperse SiO₂ nanoparticles by membrane emulsification using ideally ordered anodic porous alumina. *Langmuir*, 2004. 20(3): p. 554–555. <https://doi.org/10.1021/la030314a> PMID: 15773073
52. Park S.K., Do Kim K., and Kim H.T., Synthesis of monodisperse SiO₂ and TiO₂ nanoparticles using semibatch reactor and comparison of parameters effecting particle size and particle size distribution. *Journal of Industrial and Engineering Chemistry*, 2000. 6(6): p. 365–371.
53. Júnior J.A.A. and Baldo J.B., The behavior of zeta potential of silica suspensions. *New Journal of Glass and Ceramics*, 2014. 4(02): p. 29.
54. Xu R., Progress in nanoparticles characterization: Sizing and zeta potential measurement. *Particuology*, 2008. 6(2): p. 112–115.
55. Singh J., et al., 'Green' synthesis of metals and their oxide nanoparticles: applications for environmental remediation. *Journal of nanobiotechnology*, 2018. 16(1): p. 1–24.
56. Shah M., et al., Green synthesis of metallic nanoparticles via biological entities. *Materials*, 2015. 8(11): p. 7278–7308. <https://doi.org/10.3390/ma8115377> PMID: 28793638
57. Kim J.M., et al., Control of hydroxyl group content in silica particle synthesized by the sol-precipitation process. *Ceramics International*, 2009. 35(3): p. 1015–1019.
58. Li X., et al., Durable superamphiphobic nano-silica/epoxy composite coating via coaxial electrospraying method. *Applied Surface Science*, 2018. 436: p. 283–292.
59. Ek S., et al., Determination of the hydroxyl group content in silica by thermogravimetry and a comparison with 1H MAS NMR results. *Thermochimica acta*, 2001. 379(1–2): p. 201–212.
60. Wang B.-X., Zhou L.-P., and Peng X.-F., Surface and size effects on the specific heat capacity of nanoparticles. *International journal of thermophysics*, 2006. 27(1): p. 139–151.
61. El Far B., et al., Investigation of heat capacity and viscosity enhancements of binary carbonate salt mixture with SiO₂ nanoparticles. *International Journal of Heat and Mass Transfer*, 2020. 156: p. 119789.
62. Li Z., et al., Effects of SiO₂ Nanoparticle Dispersion on The Heat Storage Property of the Solar Salt for Solar Power Applications. *Energies*, 2021. 14(3): p. 703.