

Review

Extraction and Synthesis of Silicon Nanoparticles (SiNPs) from Sugarcane Bagasse Ash: A Mini-Review

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Abstract: This current study reviews the utilization of the traditional extraction methods and latest findings in extraction of silica from agricultural wastes, in particular, sugarcane bagasse, using inorganic acids to produce nano-silicon. The three key processes discussed in detail include electrochemical, ball milling, and sol-gel processes. The sugarcane bagasse has been identified as the cheapest source of producing silica from the potential raw material for the preparation of nano-silicon. The acid-base extraction and precipitation methodology involves the use of bases like sodium hydroxide (NaOH) and potassium hydroxide (KOH), and acids such as hydrofluoric acid (HF), sulphuric acid (H₂SO₄), nitric acid (HNO₃), and hydrochloric acid (HCl) for the treatment of the ash. Sugarcane bagasse has notably emerged as an excellent and sustainable source of both tailored silica particles and bioenergy production. The ability to manipulate the engineered silica particles at the nano-level from sugarcane bagasse-based silica is explained in detail. Silica is a significant raw material with various industrial applications, with much research underway to extract it efficiently from industrial agro-waste, such as sugarcane bagasse. The production of highly pure silicon nanoparticles from sugarcane bagasse ash will serve as an important synthetic route in lowering the manufacturing costs and providing a low-cost polycrystalline silicon semiconductor for niche application in thin film solar technology.

Keywords: sugarcane; silica; SiNPs; silicon; green technology



Citation: Seroka, N.S.; Taziwa, R.T.; Khotseng, L. Extraction and Synthesis of Silicon Nanoparticles (SiNPs) from Sugarcane Bagasse Ash: A Mini-Review. *Appl. Sci.* **2022**, *12*, 2310. <https://doi.org/10.3390/app12052310>

Academic Editor: Anming Hu

Received: 14 January 2022

Accepted: 14 February 2022

Published: 23 February 2022

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1. Introduction

Valorization of sugarcane bagasse has been studied extensively over the years, with its niche applications in the sugar industry and bioenergy production. Silicon dioxide (SiO₂), often known as silica, is a useful inorganic multifunctional chemical substance that is one of the basic materials. Silica can be found in nature as quartz, sand, or flint. Gel and amorphous forms are also possible, with both crystalline and amorphous forms found in the earth's crust [1,2]. In their study, El Sayed and El-Sammi reported numerous silica content in different sources: Sorghum (88.75%), wheat (90.56%), corn (64.32%), bamboo (57.40%), bagasse (73.00%), lantana (23.38%), sunflower (25.32%), rice husk (93.00%), rice straw (82.00%), and bread fruit tree (81.80%) [3].

The silica comes from the soil in the form of silicic acid, which the sugarcane plant absorbs and collects around the cellulose micro-compartments. The quantity of silicon in the soil influences silica concentration. Sugarcane roots play a key role in absorbing silicic acid from the soil and delivering it to the shoots, where it is stored as amorphous silica. Amorphous silica predominates in sugarcane bagasse ash with other metallic contaminants [2,3].

In this study, the use of bases such as *NaOH*, *KOH* and acids like *HF*, *H₂SO₄*, *HNO₃*, and *HCl* for the pre-treatment of the ash, and yield silica with desirable properties. The

sugarcane bagasse ash is rich with silica of about 73%, and it is economically feasible due to the conversion of raw material to the production of silica gels and powders [4,5]. The sugarcane bagasse has been investigated as the potential raw material and source of sugar, juice, and fuel in the ethanol industry (shown in Figure 1) and valuable material in the cementitious industry [6].

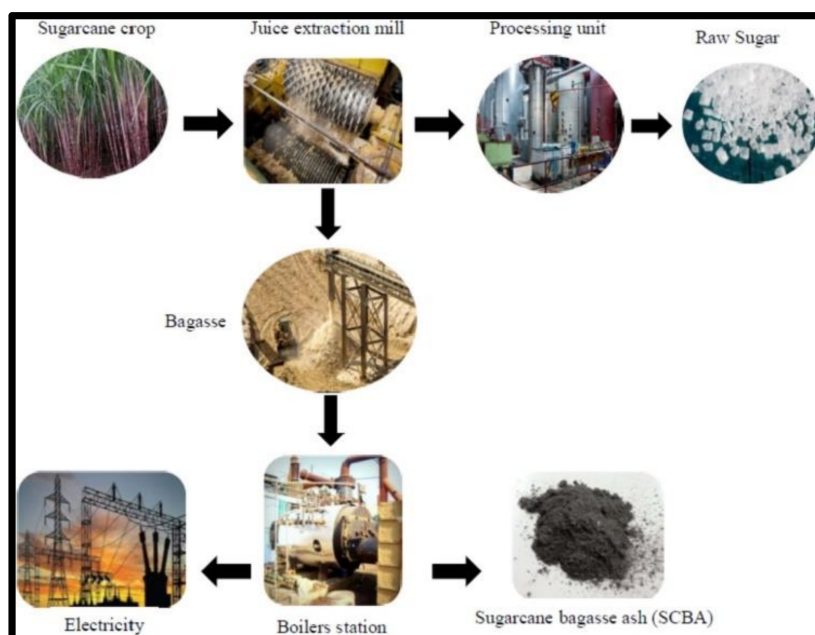


Figure 1. Flow diagram of sugarcane bagasse ash [6,7].

Many industrial processes (shown in Figure 1) in the transformation of sugarcane into sugar and ethanol, namely, the burning process of the biomass for energy production, result in ashes with high impurity content, such as iron and aluminum oxides, hindering the process of obtaining silica with satisfactory purity values [6]. Thus, the resulting ashes require additional purification processes HCl acid leaching allied or not to a sol–gel method [6,7].

The silica nanocomposites (soluble silicates) are widely used in the glass, ceramic, and cement industries as a major component and in cosmetic, pharmaceutical, and detergent industries as bonding and adhesive agents. Notably, silica has been used as a major precursor in a variety of applications as inorganic and organometallic materials, which have desirable applications in synthetic chemistry as a catalyst, coating for electronic optical materials, and thin films [7].

Sugarcane Bagasse in South Africa

The sugarcane, shown in Figure 2, is an economical and strategic crop for the Mpumalanga and Kwazulu Natal, where the production is located, it is comprised of a substantial percentage of field crop gross farming income across the two provinces. To date, about 22,949 registered sugarcane growers annually produce an average of 20 million tons of sugarcane from 14 million supply areas, ballooning from southern Kwazulu-Natal to the Mpumalanga Lowveld [8].

Presently, the growers are represented by the Southern African Cane Growers Association (SACGA) and the South African Farmers Development Association (SAFDA). Thus, there are approximately 21,581 small-scale growers, of whom about 12,019 delivered cane in the 2018/2019 season, with the production at 9.33% of the total crop. This is composed of 116 consolidated units, including co-operatives, trusts, and projects, with the make-up of 7536 individual beneficiaries. There are 1368 large-scale growers, including 345 black

emerging farmers, and they produce 81.17% of total sugarcane. Milling companies with their own sugar estates produce 9.17% of the crop [9].



Figure 2. Images of a typical sugarcane plantation, stalks, and bagasse from the South African sugar industry [8].

Advanced studies have been ongoing to investigate the various ways for the production of silica from sugarcane bagasse using simple processing routes. The traditional routes moderately utilized for agricultural wastes to silica include synthetic routes, such as acid treatment, calcination, partial burning, leaching, enzymatic treatment, pyrolysis, hydrolysis, and sol–gel. Traditionally, silica is produced by reaction of sodium carbonate powder and quartz sand at higher temperatures to form sodium silicate, which will then react with sulfuric acid to precipitate silica [10].

This method is considered hazardous to the ecosystem since most of its by-products (sodium sulphate, carbon dioxide, and lots of wastewater) are detrimental to the environment. In this review, the production of silicon nanoparticles from nano-silica is explained in detail, emphasizing the importance of turning waste into wealth. Interestingly, biomass is in abundance and serves as the future source of renewable energy reservoirs [11].

2. Extraction of Silica

The extraction of silica from various agro-wastes has been acknowledged by many researchers across the globe. The agricultural wastes have been identified as the potential raw material for the preparation of silicon composites. The sugarcane bagasse ash is an abundant by-product of agro-food waste materials. These waste materials pose a threat to the environment and thus require proper utilization to get valuable products. It is thus the cheapest source of silica production, and the chemical compositions of a typical sugarcane bagasse ash with geographical locations are shown in Table 1. Moreover, the benefits include: Easy to handle and affordable. It is noteworthy to realize the potential reasons to have several methods to produce silica from various agro-wastes. These include, low material consumption, thus reduced costs, the high silica content in the agro-wastes, relative silica quality, nature of the material (amorphous), energy content, and eventually, low energy consumption [12,13].

Table 1. Elemental composition (%) of sugarcane bagasse ash from various countries: Analysis and authors.

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3/SO_4	K_2O	Loss of Ignition (LOI)	Country	Authors
62.1	5.42	5.54	1.0	1.12	-	2.22	-	Uganda	(Basika, et al. 2015). [14]
84.0	1.7	1.1	0.5	0.6	-	0.5	3.1	South Africa	(Aboyade et al. 2011) [15]
72.8	5.5	6.4	3.8	2.3	-	2.7	3.7	Columbia	(Torres Agredo et al. 2014) [16]
96.2	1.7	0.2	0.1	0.1	0.1	0.3	1.04	Brazil	(Sales and Lima 2010) [17]
31.41	6.02	7.57	16.06	1.07	0.78	1.58	32.2	Brazil	(Castaldelli et al. 2013) [18]
67.82	2.56	6.33	1.54	2.03	-	2.87	2.31	Thirukovikur	(Hariharan et al. 2014) [19]
87.59	0.67	0.57	2.59	1.65	0.003	3.64	NA	India	(Modani and Vyawahare 2013) [20]
62.43	6.98	4.28	11.8	2.51	1.48	3.53	4.73	India	(Kawade, Rathi, and Girge 2013) [21]
66.89	29.18	29.18	1.92	0.83	0.56	NA	0.72	India	(Hussein et al. 2014) [22]
41.15	2.70	7.00	3.20	0.12	0.03	8.75	17.7	Nigeria	(Otoko 2014) [23]
77.25	4.21	6.37	4.05	2.61	0.11	2.34	1.40	Sudan	(Hussein et al. 2014) [24]
72.85	6.96	1.08	9.97	6.49	NA	6.71	4.23	Nigeria	(Abdulkadir, Oyejobi, and Lawal 2014) [25]
44.70	2.90	2.40	14.9	3.50	NA	4.40	16.7	Iran	(Abbasi and Zargar 2013) [26]

SiO_2 The table above shows the chemical make-up in the extracted silica from sugarcane bagasse ash from various countries, and it is quite evident that it is composed mostly of SiO_2 . In South Africa, the bagasse constitutes approximately 84% of SiO_2 , the third-highest after India and Brazil with 87.59% and 96.2%, respectively. This makes sugarcane bagasse an ideal source of SiO_2 to investigate and explore for further studies [14,16,26].

The calculation below was carried out to find the percentage yield from the chemical treatment reported in [27]. The results from XRF, XRD, and SEM showed the metal oxides present and key findings on silica, which were calculated using the approximation calculation method [27].

$$100 \text{ g of SBA introduces approximately } 76.34 \text{ g of } SiO_2 \quad (1)$$

$$\text{Therefore, unknown (X) amount of SCBA will introduce } 73.21 \text{ g of } SiO_2 \quad (2)$$

$$\text{The aforementioned implies, } = \frac{100 \times 73}{76.34} = \frac{7300}{76.34} = 95.625 \text{ g of SCBA} \quad (3)$$

$$\text{For, } Al_2O_3 \text{ since } 100 \text{ g SCBA introduces } 6.7 \text{ g of } Al_2O_3, \text{ then: } 95.625 \text{ g of SCBA will introduce } = \frac{95.625 \times 6.7}{100} = \frac{640.688}{100} = 6.407 \text{ g of } Al_2O_3 \quad (4)$$

$$Fe_2O_3: \text{ Since } 100 \text{ g SCBA introduces } 6.3 \text{ g of } Fe_2O_3, \text{ then: } 95.625 \text{ g of SCBA will introduce } \frac{95.625 \times 6.3}{100} = \frac{602.438}{100} = 6.024 \text{ g of } Fe_2O_3 \quad (5)$$

$$\text{CaO: Since 100 g SCBA introduces 2.8 g CaO, then: 95.625 g of SCBA will introduce} = \frac{95.625 \times 2.8}{100} = \frac{267.75}{100} = 2.678 \text{ g of CaO} \quad (6)$$

$$\text{MgO: Since 100 g SCBA introduces 3.2 g MgO, then: 95.625 g of SCBA will introduce} = \frac{95.625 \times 3.2}{100} = \frac{306}{100} = 3.06 \text{ g of MgO} \quad (7)$$

$$\text{P}_2\text{O}_5: \text{ Since 100 g SCBA introduces 4.0 g P}_2\text{O}_5, \text{ then: 95.625 g of SCBA will introduce} = \frac{95.625 \times 4.0}{100} = \frac{382.5}{100} = 3.825 \text{ g of P}_2\text{O}_5 \quad (8)$$

$$\text{Na}_2\text{O: Since 100 g SCBA introduces 1.1 g Na}_2\text{O, then: 95.625 g of SCBA will introduce} = \frac{95.625 \times 1.1}{100} = \frac{105.188}{100} = 1.052 \text{ g of Na}_2\text{O} \quad (9)$$

$$\text{K}_2\text{O: Since 100 g SCBA introduces 2.4 g K}_2\text{O, then: 95.625 g of SCBA will introduce} = \frac{95.625 \times 2.4}{100} = \frac{229.5}{100} = 2.295 \text{ g of K}_2\text{O} \quad (10)$$

$$\text{LOI : Since 100 g SCBA introduces 0.9 g LOI, then: 95.625 g of SCBA will introduce} = \frac{95.625 \times 0.9}{100} = \frac{86.063}{100} = 0.861 \text{ g of LOI} \quad (11)$$

2.1. Electrochemical Process

The electrochemical procedure is considered one of the most versatile techniques to synthesize silicon nanoparticles (SiNPs). The procedure involves the filling of a Teflon cell with a mixture of aqueous hydrofluoric acid (HF) and ethanol, subsequently followed by etching of a silicon wafer carried out under steady current supply, as shown in Figure 3 [28]. The reaction mechanism of diluting HF for silicon wafer etching is presented below:

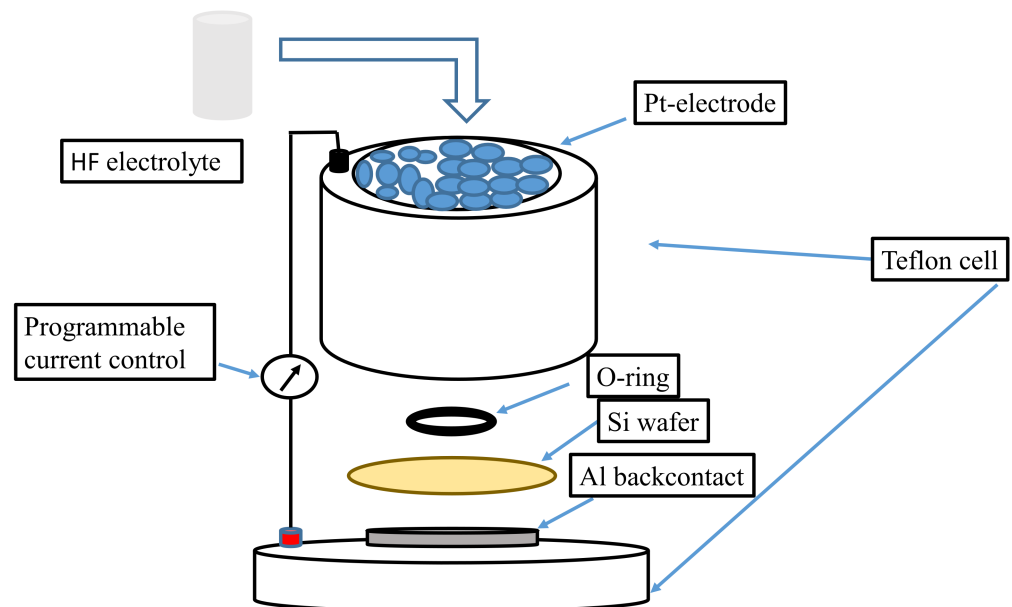
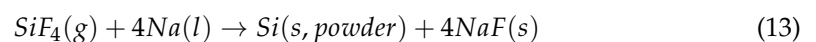


Figure 3. Electrochemical etching set-up.

The fundamental approach is the perspective of producing porous silicon (PSi), traditionally known as silicon nanocrystal thin film, which surpassed photo luminescent SiNPs developed from vanostatic adonization.

Triumphs and Challenges

The distortion or break-up treatment is performed on an etched PSi layer for sonication procedure in order to obtain the desired quantum-confined colloidal silicon nanoparticles

(SiNPs). Furthermore, it is not easy to manipulate and alter the properties of PSi thin-film and surface morphology due to the irreversible effect caused by the electrolyte composition, silicon dopant type, dopant concentration, and etching time. However, ethanol can alter and prevent the bubble break-up and reduce the hydrophobicity, which ultimately leads to an effective pore formation, an advantageous feature, and consequently, uniformity retained as a result of hydrogen-terminated silicon nanocrystals [29–31].

2.2. Ball Milling Process

Ball milling is a popular method because of its simplicity and requiring relatively inexpensive equipment to operate and can be deployed on a wide range of other materials. Nano-crystalline materials can be successfully produced using the aforementioned process. Lam et al., 2000, synthesized ultra-fine SiNPs with 5 nm using solid graphite (C) in concurrent with silicon dioxide SiO_2 in a planetary ball miller shown in Figure 4 for about 7–10 days on a larger scale. The mixture was loaded on a stainless-steel vial together with stainless-steel balls (7.5 mm diameter), and the molar ratio employed was 1:1 graphite- SiO_2 as shown in the reaction mechanism below [31].

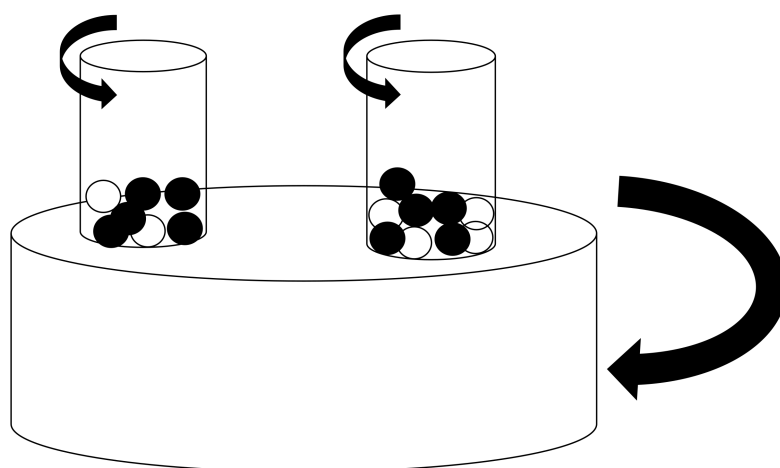
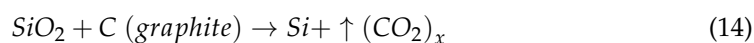


Figure 4. Planetary ball mill for the preparation of SiNPs.

The content was then sealed with a Viton O-ring. However, the vial was first purged with argon to remove other gases, with the remaining argon set to atmospheric pressure. After a period of 7–10 days, respectively, the powders (milled) were then annealed in a hydraulic press for 48 h at 150 °C under a loading of 30 kgf/mm². In addition, the annealed powders were then put back into a vial and further milled for another 2 more hours to break up the pressed tablet into powder form [31].

The resulted NPs were reported to have been covered with an amorphous SiO_2 layer of 1 nm in thickness and produced a multi-peak PL spectrum as a result of a wide range of particle sizes present.

Triumphs and Challenges

The physical methods usually are capable of achieving size controllability of the as-synthesized SiNPs. The major drawback is that the productivity is not scalable and the chemistry of Si QDs to be stabilized is not well established [27]. Furthermore, the presence of aggregates presents a complex and coarse shape apart from the size distribution. Thus, it limits the utilization of ball milling synthetic route in spite of its convenience and inexpensiveness [31].

2.3. Sol–Gel Process

The sol–gel procedure is a wet chemical approach traditionally known as chemical solution deposition. It involves, several steps, namely, hydrolysis and polycondensation, gelation, aging, densification, and crystallization. The processing of inorganic ceramic and glass materials was first conducted as early as the mid-1800s by Ebelman and Graham's studies on silica gels [32]. The process mainly involves alkaline extraction, followed by acid precipitation.

Sugarcane bagasse is cleaned and made moisture-free by drying. Additionally, studies have reported that acid pre-treatment is one of the effective ways to remove of ionic impurities from sugarcane bagasse [33].

Therefore, 1 M *HCl* is used for pre-treatment shown in Figure 5, in a water bath and heated at 75 °C. The sample is subsequently filtered numerous times to discard metallic ions and further dried in an oven. The as-obtained sugarcane bagasse ash is then immersed in 1 M *NaOH* and refluxed for an hour at 90 °C to produce sodium silicates solution from the sugarcane bagasse, as shown in the following equation [33,34].

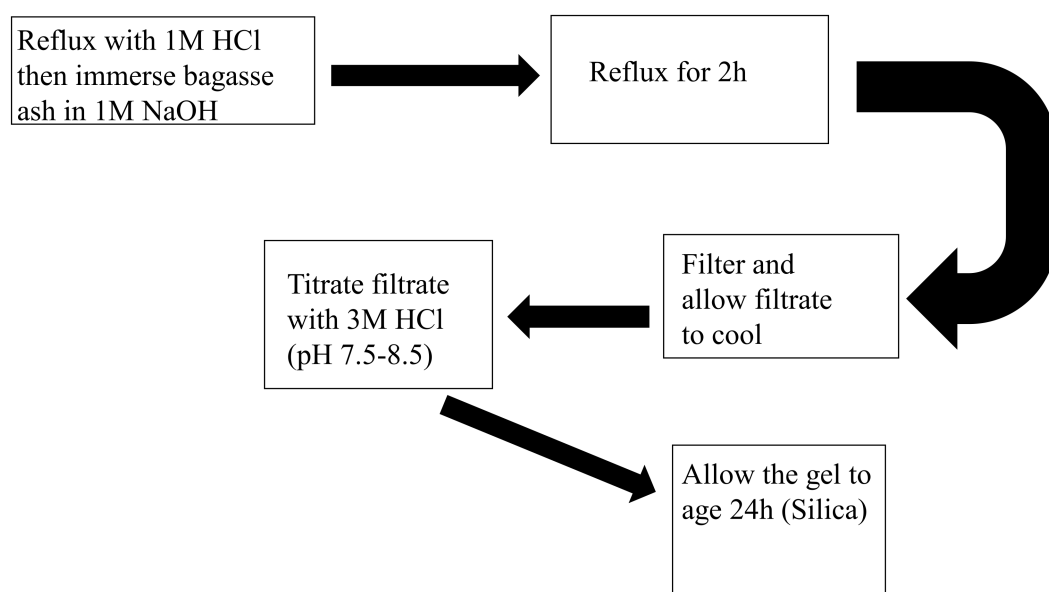
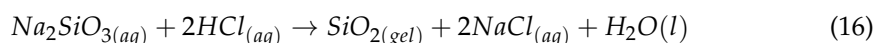
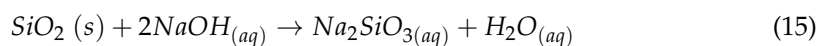
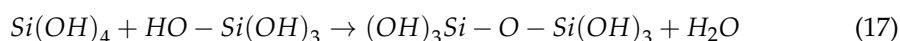


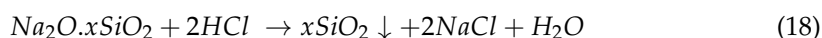
Figure 5. Sol gel method for silica preparation.

The key findings of the investigation were the observations made during the hydrolysis of tetraethyl orthosilicate (TEOS), $\text{Si}(\text{OC}_2\text{H}_5)_4$, under acidic media yielded SiO_2 in the form of a “glass-like” material [35]. Roy and co-workers did another breakthrough study where they highlighted the potential for achieving desired and efficiently high levels of homogeneity in colloidal gels. They used the sol–gel method in the 1950s and 1960s to synthesize a large number of unique ceramic oxides of novel chemical make-up, such as Al, Si, Ti, Zr, and others, which could not be achieved by other ceramic methods [35].

The high purity silica xerogels were prepared from bagasse ash to form sodium silicate by the sol–gel method. Subsequently, the mixture was treated with acid for gelating formation, whereby condensation reaction, the siloxane linkage between surface silanol groups as shown in the following reaction mechanism [36];



The precipitation procedure with the pH was maintained at >7 [35]. The sodium silicate solution with the hydrochloric acid process can be shown as:



Moreover, purification with demineralized water was found to be successful for the purity as high as 99 wt%. The structural properties indicated that the as-prepared silica xerogels were amorphous in nature [37].

Triumphs and Challenges

The chemical methods, however, showed that there is room to manipulate the SiNPs by fine-tuning the synthesis and achieve the desired properties via surface modification and controllable particle size distribution of Si Quantum Dots. However, the question of purity always arises from residual side products. The high yield and desirable uniform properties have attracted researchers worldwide to produce Si QDs using electrochemical techniques under certain conditions from porous silicon. The shape and size distribution, as well as particle size control are still a major challenge for this technique [38,39].

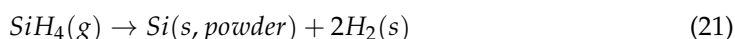
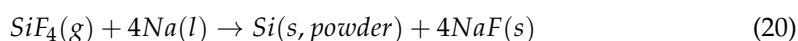
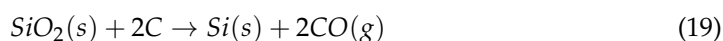
Several methods have been utilized by many researchers to study the production of nanoparticles from various feedstock. Basically, the sol-gel method is most preferred for this current study as it allows for altering of the materials from the nano-level to achieve desirable properties. Silicon nanoparticles possess high physical characteristics, outstanding opto-electronic properties (i.e., photoluminescence), active surface state, and biocompatibility, making them an ideal material and attractive to be utilized in solar cell fabrication [40,41].

3. Reduction of Silica into Silicon Nanoparticles

Below is the discussion of two methods used to reduce silica to silicon, including carbothermic and magnesiothermic reduction.

3.1. Carbothermic Reduction of Silica to Silicon

Carbothermic reduction is traditionally an industrial procedure used to manufacture-grade silicon dioxide in an electric arc furnace according to the simplified reaction Equation (19) below. The method involves high temperatures (2000 °C) and high-energy consumption, shown in Figure 6. The flow chart displays the processes involved to get high purity silica from precursor materials to silicon, using the synthetic reduction routes. Some other methods involve tetrafluoride shown in (20) similar to (c) and (b) decomposition of silane (22), however, they might not be economically viable [42–44].



The electric arc furnace requires about 1900 °C to melt sand, which translates to 50 kWh of energy for a kilogram of sand. In addition, for 60,000 tons of metallurgical-grade silicon expected to be produced annually, the required energy could be 30 TWh. Therefore, it is notably evident that the aforementioned process is energy-intensive, making it quite expensive as well as environmentally unsustainable.

Hence, it is worth investigating other alternative sources for silicon, agricultural wastes (sugarcane bagasse). The carbothermic procedure involves waste product on waste, which is advantageous for this route, synthesized activated carbon from waste material. Recently, studies have reported the use of the microwave process for carbothermic reduction of silica to silicon [44,45].

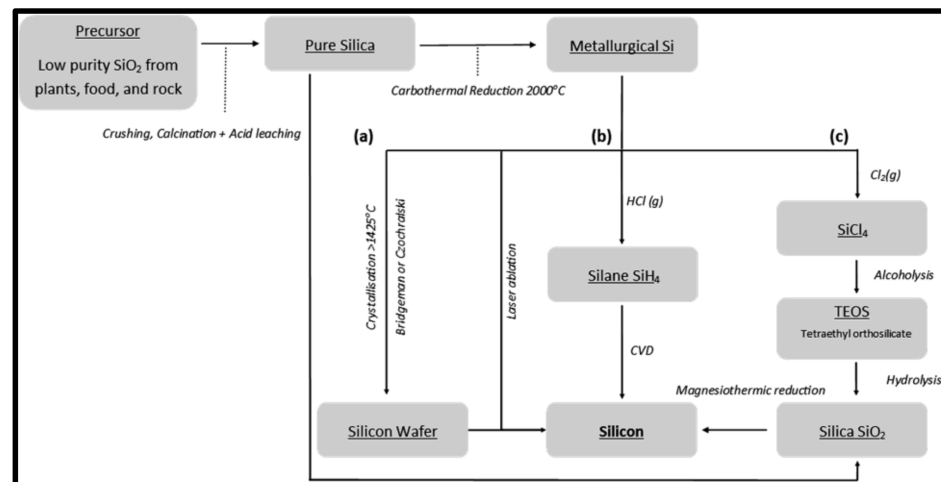
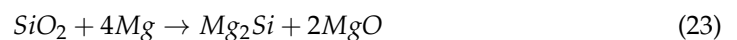


Figure 6. Flow chart of existing bulk silicon synthesis routes, including magnesium reduction [45].

3.2. Magnesiothermic Reduction of Silica to Silicon

The metallothermic reduction of silica via magnesiothermic reduction procedure leads to the formation of silicon using very low temperatures and reaction time. The procedure is not energy-intensive and thus inexpensive. The progress of the reaction depends on the experimental conditions shown in Figure 6, with temperatures below the melting point of magnesium of 650 °C, moreover, in a solid-state reaction (2) dominates [46,47].



The magnesiothermic reduction has shown the potential to produce silicon from silica in the temperature range of 500 and 950 °C, which allows template-assisted design of silicon structures. Furthermore, the method has demonstrated the ability to preserve structural and intricate features in the as-synthesized silicon as small as 15 nm. The production of pure silicon requires one last step, where nitric acid (HNO₃) and hydrochloric acid (HCl) are added to remove any unreacted silica and excess magnesium present in the sample, essentially, other studies report the use of two acids aqua regia than single acid addition, consequently, leaving silicon replica behind with improved and higher surface area than the starting template [48].

4. Purification of Silicon

Production of silicon from several agricultural wastes is not usually obtained directly without passing through the refining process. Thus, purification of silicon is an essential part, especially in industrial solar-grade (SoG)-silicon. Due to the shortage of semiconductor-grade, which is expensive, it has been a great challenge for its production [49,50].

This later led to the new ways of upgrading the metallurgical-grade silicon at a lower cost though at the expense of loss of some of silicon. The upgraded metallurgical-grade silicon (UMG-Si) generally contains impurities, which affects the photovoltaic performance, namely, short-circuit current (JSC), open-circuit voltage (VOC), fill factor (FF), and power conversion efficiency in silicon-based solar cells [51–54].

Furthermore, the phosphorus diffusion gettering process has been widely utilized to improve the performance of Si solar cells. Moreover, the enhanced performance in the photovoltaic technology has been mainly due to improving the electrical properties of UMG-

Si wafers and solar cells. The minority-carrier recombination lifetime and photovoltaic performance degradation of p-type silicon solar cells, as well as the effects of metallic contaminant type and concentration thereof (Al, Cu, Ni, and Fe), have been reported [55].

Therefore, the stable SoG-Si has led to the quest to find suitable purification methods and to reduce the production cost minimally without affecting the desired properties of the built solar cells. It is worth noting that these several purification methods are usually the simple preparation of SoG-Si from lower grades, mostly the MG-Si. Consequently, it has been shown that heat treatment could be used to essentially modify the morphology of purified silicon.

Presently, the solvent refining process has been proved to be an important purification method that is beneficial to the cost due to its high purification efficiency and low processing temperature. It usually involves alloying silicon with another element to enable the solvation and solidification with recrystallization of silicon from the solvent at a much lower temperature than the melting point of silicon, subsequently followed by separation of the crystallized silicon [56,57]. Several other refining methods include directional solidification, fractional melting, leaching, slag treatment/gas blowing, electron beam melting, etc., [57].

5. Conclusions

The review provides information about the importance of conventional procedures to produce nano-silicon from sugarcane bagasse. The electrochemical process can produce highly porous quantum-confined colloidal silicon nanoparticles. The disadvantage arises from the overall material properties because it is not easy to manipulate due to the irreversible effect caused by electrolyte composition, the ball milling procedure is popular for its relatively simplistic (ease of operation) and inexpensive approach to producing sizeable silicon nanoparticles, however, the major limitation is the inability of scalability and the chemistry of Si quantum dots (stability). Another conventional method discussed is the sol-gel procedure with the ability to fine-tune the material property via surface chemistry (modification) and controllable particle size distribution, although the purity factor has always been the major drawback for this method arising from residual by-products. Interestingly, a window of opportunity for improvement still exists for the three discussed procedures for the production of highly pure silicon nanoparticles from sugarcane bagasse ash, which will serve as an important synthetic route in lowering the manufacturing costs and providing low-cost polycrystalline silicon semiconductors for application in thin-film solar technology.

Author Contributions: N.S.S. conceptualized and drafted the original version of the manuscript, R.T.T. assisted with development and designed the presented idea. L.K. verified the analytical methods and revised for contribution to knowledge. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Research Foundation (NRF), South Africa, grant number: 120375 and Tertiary Education Support Program (TESP), Eskom Holdings SOC Limited Reg No 2002/015527/06.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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