Review

Potential of producing solar grade silicon nanoparticles from selected agro-wastes: A review


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Abstract

The U.S. Energy Information Administration (EIA) stated that Nigeria generates around 3080 MW of electricity but with actual estimated demand of 10,000 MW. Due to the low electricity generation, total energy consumption profile of Nigeria showed that about 99% of the energy consumed is derived from fossil fuels which invariably contribute to greenhouse gases emission. Electricity, if readily available at low cost, can easily replace the fossil fuels which pose adverse effect on the citizen and climate. Solar photovoltaic is identified as an effective renewable energy source that has proven to be a promising candidate for provision of clean and sustainable electricity. Silicon is the leading commercialized terrestrial PV material for making solar cell due to its relative efficiency. This review work highlights the viability of using abundant agricultural wastes in Nigeria to produce nano-sized solar grade silicon employing methods that will require less energy. Details of previous silicon (nanoparticles) synthesized from agricultural wastes are dissected. Production of silicon nanoparticles from this origin could provide low cost solar grade silicon compared with high temperature robust methods currently being used to obtain them. Hence various methods of producing nanoparticles are highlighted.

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1. Introduction

Energy is very crucial to the sustainability of our societies (Chendo, 1994), without which life could be unconceivable with a lot of absence in our world. Its supply has been seen as future problem consequently drawing attention of all nations because human welfare in our modern life is intimately related to the quality and quantity of energy utilized (Hasan et al., 2012). As projected by several organizations, Fig. 1 shows the world electricity generation for more than two decades from 1990 which increases across the continents owing to people demand for more energy. Electricity distributed via national grids has been dominated by fossil fuels among the major sources of electricity which include coal, natural gas, petroleum, nuclear, hydroelectricity and renewables, as shown in Fig. 2.

Combustion of fossil fuels to unlock the energy stored in them has paved way for emission of greenhouse gases (GHGs) which contribute significantly to global warming (International Energy...
Solar photovoltaic (PV) energy has been realized as a gorgeous and effective renewable energy resource that could provide clean and sustainable power generated from the inexhaustible solar energy (Goetzberger et al., 1998; Kumar and Rosen, 2011; Muneer et al., 2003; Parida et al., 2011; Tsoutsos et al., 2005; Shah et al., 1999). The utilization of this enormous gift of nature was showcased fourteen years ago in solar buildings (Masuki, 2011). Fig. 5 shows the applications of solar PV in solar community settlement (Glaser, 2009), traffic light (FHKE, 2007), aerospace (Vuille, 2014; NASA, 2000), automobile (Prince Arutha, 2014), solar car mobile station (Tatmouss, 2010) and marine (Kołodziejczak-Radzimska and Jesionowski, 2014).

The energy available in the Sun is more than 10,000 times that required on the earth planet (El Chaar et al., 2011); if harnessed will be sustainable and is still the cheapest in areas where its reception is high since it costs nothing but space and gadgets (efficient PV module and storage facilities) required to tap into it. Krauter and Ruther (2004) also calculated the reduction in GHGs emitted by replacing diesel generating engines with PV technologies in Brazil while Peng et al. (2013) examined the sustainability and environmental performance of electricity generation systems based photovoltaic technologies. Consequently, introduction of this green energy (integrated with others) will minimize the side effects of climate change (Li et al., 2016; Liu et al., 2013; Lorenz and Kandelbauer, 2014).

The average radiation in tropical and sub-tropical regions in developing countries is between 1600 and 2200 kW h/m² annual global radiation (U.S. Energy Information Administration, 2011). Nigeria is located within this region as shown in Fig. 6 which makes it a potential beneficiary of this gift of nature and the prospect for PV market in the country has been studied by Adurujia et al. (1998). It is evident from Fig. 7 that Nigeria has not been categorized among the countries utilizing its solar energy potential but government’s Electricity vision 30–30–30 is revealed in Nigerian Sustainable Energy for All (SE4ALL) action agenda (Liu et al., 2005). Researchers and governments across the world are working assiduously in order to improve the efficiency of gadgets required for concentrating heat and generating electricity from the Sun (U.S. Department of Transportation 2012; Chanap, 2012; Hutmacher, 2000; Laurenzi and Marchetti, 2012; Li et al., 2008; Loos and Springer, 1983).

Silicon is the leading commercialized PV material for non-terrestrial application due to its relative efficiency along with cadmium telluride (CdTe), and copper-indium-gallium-diselenide (CIGS) Pizzini, 2009. Researchers and industries later investigated into thin film technologies for materials reduction and improvement of the cell performance (Gorter and Reinders, 2012; Madakson et al., 2012; Majid et al., 2012). Manufacture of solar grade silicon (SoG-Si) initially depended on by-products from electronic grade silicon (EG-Si) production which make it to be very expensive. The cost was later reduced by refining metallurgical grade silicon (MG-Si). The various methods of manufacturing low-cost solar-grade silicon have been reviewed (Mauk, 2003; Bathey and Cretella, 1982). Untila and Zaks (2011) reviewed scientific and technical research works accomplished on silicon solar cells aimed at reducing cost of photovoltaic power. Researchers are ongoing on market introduction of cheaper and higher efficiency organic thin-film PV technologies with great optimism on recently discovered perovskites solar cells (Loh et al., 2015).

### Table 1

<table>
<thead>
<tr>
<th>Country</th>
<th>GDP (US $ billions)</th>
<th>GDP per capita (US $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>17947.00</td>
<td>51486.00</td>
</tr>
<tr>
<td>China</td>
<td>10866.44</td>
<td>6416.18</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>2848.76</td>
<td>40933.46</td>
</tr>
<tr>
<td>Nigeria</td>
<td>481.07</td>
<td>2548.2</td>
</tr>
<tr>
<td>South Africa</td>
<td>312.80</td>
<td>7575.24</td>
</tr>
<tr>
<td>Egypt</td>
<td>330.78</td>
<td>2707.09</td>
</tr>
<tr>
<td>Algeria</td>
<td>166.84</td>
<td>4152.77</td>
</tr>
</tbody>
</table>

### Fig. 3

Total primary energy consumption in Nigeria (U.S. Energy Information Administration, 2015).
Though quartz, which is a raw material for silica, is readily available in Nigeria (Merati and Eustaugh, 2007; Merati and Gasser, 2006; Michael, 2006; Murugan and Ramakrishna, 2005), the challenge of poor electricity generation in the country would not make their conversion to solar grade silicon (SoG-Si) economical because of high processing temperature requirement (Zemnukhova et al., 2012). Silicon nanoparticle production can as well be produced via several means as reviewed by Ma et al. (2006). The conversion of agro-wastes to low cost SoG-Si nanoparticles for production of cost effective solar cells could be a means of solving the environmental challenges due to inefficient waste management and energy insufficiency. In order to reduce waste generated from rice mills, rice husk has been employed to synthesize silicon by various researchers (Banerjee et al., 1982; Mishra et al., 1985; Ikram and Akhter, 1988; Nandi et al., 1991; Larbi et al., 2012; Venkateswaran et al., 2012). This has prompted this review considering numerous agricultural wastes produced in Nigeria.

This review highlights the prospect of producing silicon nanoparticles from other agricultural wastes of importance to Nigeria. Its agricultural profile will be highlighted with wastes generated from few of them. Previous works on the production of silicon from rice husks are also discussed. The prospect of using Si nanoparticles produced from this source in thin film PV production will also be enumerated.

2. Nigeria agricultural profiles and waste management

Nigeria occupies total area of 923,768 sq km with 98.59% landmass out of which 78% is agricultural land (see Fig. 8). Nigeria produces crops such as cocoa, peanuts, cotton, palm oil, maize, rice, sorghum, millet, cassava, yams, rubber; and timber (Navarro et al., 2012).

As in 2009, Nigeria generated 3.4 million tonnes of cassava peelings (Heuzé et al., 2014) and similar wastes are generated annually from the numerous agricultural produces during their domestic and industrial processing to semi-finished or finished products. Indiscriminate disposal and burning of these wastes pose major challenges to sustainable healthy environment. Some of the wastes are intentionally used as fossil fuels domestically and industrially to augment energy need at low cost but without considering their side effects on our environment. Burning the agro-wastes produces greenhouse gases (GHGs) which have adverse effect on the climate and ecosystem leading to depletion of the ozone layer and subsequently global warming (Greenhouse gas, 2015). Indiscriminate disposal in open spaces pollutes the environment with irritating odours and emission of unhealthy hazardous gases. All these unwanted products cumulatively affect the life expectancy of people (Asif and Muneer, 2007). Recycling and conversion of many of these wastes to useful products with good economic values have been the efforts of many researchers to sustain a sustainable cleaner environment.

2.1. Cassava

Typically, Nigeria is the largest producer of cassava in the world with a tonnage of about 30 million tonnes as in 2002 (Truman et al., 2004; Felix, 2005). It is cultivated across the country with the North Central Nigeria producing the largest proportion (27%) followed by South South (23%), South West (21%), South East (21%), North West (8%) and the remaining from the North East (Truman et al., 2004). In Fig. 9, a typical cassava processing route is illustrated. The cassava tubers after transporting to the processing site are processed in commercial factory (Plate A) (EKHA Agro, a Glucose Syrup producing factory, Ogun State) or small scale factory (Plate B) (Oja Tuntun, Baboko Area, Ilorin, Kwara State) to give cassava peelings (Plate C) (a dumpsite at Atiba local government, Oyo, Oyo State) which could be processed further by drying and sorting (Plate D) (Betterlife market, Isale-Osun, Osogbo, Osun State) to get dried cassava peelings (Plate E) and...
Fig. 5. Applications of PV technologies in (a and b) aviation (Vuille, 2014; NASA, 2000), (c, f and g) automobile and traffic (FHKE, 2007; Prince Arutha, 2014; Tatmouss, 2010), (d) marine (Kołodziejczak-Radzim ska and Jesionowski, 2014) and (e) community settlement (Glaser, 2009).

Fig. 6. World Map of Global horizontal Irradiation (SolarGIS, 2013).
finally cassava periderm (Plate F) which is a complete waste of no economic value.

A cassava starch production unit processing 100 tonnes of tubers per day has an output of 47 tonnes of fresh by-products which may inadvertently pose environmental challenges when carelessly disposed or left in the processing plant’s neighbourhood (Aro et al., 2010). Cassava peelings can represent 5–15% of the root which invariably means 4680 tonnes of cassava peel per annum (Aro et al., 2010; Heuzé, 2014; Nwokoro et al., 2005). The main use of this waste is for livestock feed, else it is usually burnt or left to rot away creating waste heaps around the facility or in a designated place (Heuzé et al., 2014). Cassava peels which contain cassava periderm (CP), as shown in Fig. 10, are usually discarded or burnt whenever available.

2.2. Maize

Maize is a unique plant as source of staple food for indigenous peoples in rural areas. United States and China are the major producers of maize in the world while Nigeria is the second in Africa (Maize, 2015; Badu-Apraku et al., 2014). Fig. 11 shows the various parts of a typical maize plant (on the left). Usually after the ears are harvested from Plate A, the stalks are left to decompose in situ (Plate B), grazed by cattle (Plate C) while some farmers ploughed them for another planting. The ears after harvesting (Plate E) are processed for the grains. The stalks (Plate D), cobs (Plate F) and husks (Plate G) are various wastes from the plant.

2.3. Sugarcane

Sugarcane is one of the species of tall perennial true grasses. It has stout jointed fibrous stalks rich in sucrose accumulating in the stalk internodes, thus used in sugar production (Sugarcane, 2015). Fig. 12 highlights basic domestic stages that generate sugarcane bagasse: Plate A is a sugarcane plantation at Giwa Local Government, Kaya, Kaduna State; Plates B, C and D show sugarcane processing at Orange market, Mararaba, Karu Local Government, Nasarawa State, while Plate E is the common means of selling to the consumers. The wastes from sugarcane, Plates D and F can be used as the source of sugarcane bagasse. The bagasse could be obtained either by mechanical milling or by direct chewing.
3. Synthesis of nanoparticles

The introduction of thin films PV technologies has recently been appreciated to have the highest potential in cutting cost which is the main bane of thin-film silicon PV technologies (Martin et al., 2004). The main advantage of these technologies is materials reduction unlike the wafer silicon (Sopori, 2007). Other merits include high product quality with relatively high efficiency, low energy needs and large area production (Loos and Springer, 1983). The advent of nanotechnology has improved manufacturing of several products with higher efficiency because of improved materials properties (Pokropivny et al., 2007).

Nanoparticles can be produced through various known methods categorized as either “bottom-up” or “top down” (De Castro and Mitchell, 2003; Yadav et al., 2012; Bhushan, 2004; Kulkarni, 2009; Overney, 2010; Robert and Nguyen, 2008) depending on whether the materials are made from elemental basis via chemical processes or reduced from its bulk state via mechanical milling or chemical attrition processes. Bottom-up nanoparticle synthesis is achieved via pyrolysis, solvothermal reaction, inert gas condensation, sol-gel fabrication and structured media while top-down methods are accomplished majorly by milling and attrition (Overney, 2010). The methods employed include laser ablation of solid targets (Niu et al., 2010), plasma- or laser-induced reactions of gaseous mixtures (Tao et al., 2012; Song et al., 2007; Remnev and Pushkarev, 2004), ball milling (Luo et al., 2010; ELECTRON MICROSCOPE; Merati et al., 2003), self-propagating high temperature synthesis (Yermekova et al., 2010a; Yermekova et al., 2010a, 2010b; Moskovskikh et al., 2013), sol–gel (Wang et al., 2001; Kim et al., 2009; He et al., 2006; Raman et al., 2005; Kandelbauer, 2014), hydrolysis (Kumar et al., 2012), spray drying of solutions (Song et al., 2008), Precipitation (Sudirmana et al., 2012), pyrolysis (Surovikin et al., 2010) and chemical vapour decomposition at low pressure (Legrand and Sénémaud, 2003).

Table 2 shows the summary of some synthesized nanoparticles giving brief highlights of the starting materials, reagents used, methods used, and final products with particle sizes in nano scale. The table shows that agricultural waste has been utilized to...
synthesize nanoparticles as low as 6 nm while microporous nanocrystalline silicon of less than 2 nm has been obtained through reduction of silica with magnesium at temperature of 650 °C.

The methods employed for synthesis of silicon nanoparticles could be categorized into physical, chemical, physiochemical, and electrochemical (Kumar, 2007). The physical methods could be by implantation or ablation; combustion, thermal decomposition, microwave plasma, gas-evaporation and chemical vapour deposition (CVD) are physicochemical methods; the chemical methods utilize reduction procedures, while electrochemical method is an etching procedure via electrodeposition and ultrasonic fracturing.

\[ \text{SiO}_2(g) + 2\text{Mg}(g) \rightarrow \text{Si}(s) + 2\text{MgO}(s) \]  

Fig. 11. Parts of a maize plant.

Fig. 12. Sugarcane plantation and various processing stages to obtain bagasse.
4. Solar cells and silicon

4.1. Trends in PV cells

A solar photovoltaic (PV) module works by converting solar radiation directly into electricity, using semiconductor technology. Illuminating a module with (solar) light excites an electron from the valence band, makes the electron to move to the conduction band and thus creates electron–hole pair. The electron (negatively charge) and hole (positively charge) generated within the module move to the n and p surfaces, respectively. When metal contacts are applied to the two surfaces, the electrons flow in an external circuit via an applied load (Muneer et al., 2003). Razeykov et al. (2011) and Rockett (2010) have reviewed the progress made in PV technologies and challenges facing them. Silicon solar cells make up 95% of solar cells and are the most developed and commercialized types as can be seen from Fig. 13 (Pizzini, 2009).

![Fig. 13. Distribution of different semiconductors in the PV chain (Pizzini, 2009).](image)

<table>
<thead>
<tr>
<th>Starting material(s)</th>
<th>Procedural highlights</th>
<th>Product(s)</th>
<th>Particle size (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk (RH)</td>
<td>Pyrolysis, leaching, sol-gel, reduction, leaching</td>
<td>Silicon</td>
<td>70–100</td>
<td>Venkateswaran et al. (2012)</td>
</tr>
<tr>
<td>Corn tissues (leaves, roots, stalks, silks, and husks)</td>
<td>Acid pre-treatment, in-situ growth (impregnation), calcination, crystallization to</td>
<td>Porous TiO$_2$– SiO$_2$</td>
<td>13.8–20.3</td>
<td>Ma et al. (2013)</td>
</tr>
<tr>
<td>RH</td>
<td>Acid pre-treatment, combustion, leaching, pyrolysis, sol-gel</td>
<td>Silica</td>
<td>6</td>
<td>Rafiee et al. (2012)</td>
</tr>
<tr>
<td>RH (from 2 different sources)</td>
<td>Leaching, calcination</td>
<td>Silica</td>
<td>181.2–294.7</td>
<td>Carmona et al. (2013)</td>
</tr>
<tr>
<td>Corn cob</td>
<td>Pyrolysis, sol-gel, calcination</td>
<td>Silica</td>
<td>305</td>
<td>Ogunfowokan et al. (2011)</td>
</tr>
<tr>
<td>RH, rice straw (RS), sylvan horsetail, scouring horsetail and larch needles</td>
<td>Hydrolysis, calcination, metallothermic reduction to</td>
<td>Amorphous silica</td>
<td>50–200</td>
<td>Zemnukhova et al. (2012)</td>
</tr>
<tr>
<td>Corn cob</td>
<td>Precipitation</td>
<td>Amorphous silica</td>
<td>25</td>
<td>Mohanraj et al. (2012)</td>
</tr>
<tr>
<td>Rice husk, coffee husk and sugarcane bagasse</td>
<td>Biotransformation, calcination, leaching</td>
<td>Silica</td>
<td>152–254</td>
<td>Espíndola-Gonzalez et al. (2010)</td>
</tr>
<tr>
<td>Cassava periderm</td>
<td>Pyrolysis, sol-gel, calcination</td>
<td>Silica</td>
<td>62.69</td>
<td>Kandelbauer (2014)</td>
</tr>
<tr>
<td>Silica, Mg</td>
<td>Magnesoithermic reduction (see Eq. (1)), Max. Temp. 650 °C</td>
<td>Silicon</td>
<td>&lt;2</td>
<td>Yermekova et al. (2010a) and Bao et al. (2007)</td>
</tr>
</tbody>
</table>
Schneider, 2013/14; Goetzberger and Hebling, 2000; Swanson, 2006). Other types of solar cells being developed use doped semiconductor materials (like GaAs, CdTe, CuInSe2, etc.), organic semiconductor cells and perovskite which are in research stage while dye-sensitized TiO2 cells are gaining momentum (El Chaar et al., 2011; Gorter and Reinders, 2012; Lotz and Schneider, 2013/14; Lizin et al., 2012; Nunzi, 2002; Green et al., 2014). There are other technologies that have been discovered, one of such is the silicon quantum dots technology (Pucker et al., 2012; Lotz and Schneider, 2013/14; Conibeer et al., 2011, 2012; Mercaldo et al., 2009; Perez-Wurfl et al., 2009; Tayagaki et al., 2013; Hodgson et al., 2013; Lee et al., 2014; Löper et al., 2013) which has been proven to have very high efficiency (Green et al., 2014). Hybrid PV cells combine crystalline silicon with non-crystalline silicon (Itoh et al., 2001) while dye-sensitized materials (about to be deployed to the market, Fig. 14) have been introduced to solve the problems with efficiency, production cost and environmental issues (Nazeeruddin et al., 2011; Gratzel, 2003). Some researchers (Aberle, 2006; McCann et al., 2001; Catchpole et al., 2001) reviewed the outstanding thin-film crystalline silicon PV technologies that have emerged in the last decade while one of the advantages of a-Si in thin film solar technology has been reviewed by Markwart and Castaner (2003).

4.2. Production of (solar grade) silicon

Silicon has been produced majorly via carbothermal reduction (see Eq. (2)) of silicon dioxide in which intermediate reactions (that yield SiO or SiC) must be avoided. The usual starting materials for this process are chunks of quartz/quartzite, coke, charcoal and wood chips for good ventilation of the charge which yields metallurgical grade silicon (MG-Si) with a purity of 98% for which a typical analysis is 0.5% Fe; 0.4% Al; 100–400 ppm each of Ca, Cr, Mg, Mn, Ni, Ti, and V; and 20–40 ppm each of B, Cu, P, and Zr (Zulehner et al., 1977). This conventional silicon production with the reduction of silica with carbon (Koch and Clément, 2007; Braga et al., 2008; Nakajima and Usami, 2009) easily gives a by-product (CO2) that is detrimental to our environment and usually involves high temperature with high energy consumption (Yermekova et al., 2010a). Other methods in use include the metallothermic reduction of the silica (see Eq. (1)) or silicon tetrafluoride (see Eq. (3)) and decomposition of silane, e.g. SiH4 (see Eq. (4)). There are several other reactions that could give silicon but most of them are not economically viable.

\[ \text{SiO}_2(s) + 2C(s) \rightarrow \text{Si}(s) + 2\text{CO}(g) \quad (2) \]

\[ \text{SiF}_4(g) + 4\text{Na}(l) \rightarrow \text{Si}(\text{powder}) + 4\text{NaF}(s) \quad (3) \]

\[ \text{SiH}_4(g) \rightarrow \text{Si}(\text{powder}) + 2\text{H}_2(g) \quad (4) \]

Semiconductor/electronic grade silicon (EG-Si), which differ from solar grade silicon (SoG-Si) Pizzini, 2009; Saravanan and Sheeba, 2012, is expensive while metallurgical grade (MG) silicon's composition is not suitable for solar application but somewhat cheap. Hence most of the SoG-Si produced has been achieved by upgrading MG-Si. Various methods (see Fig. 15) for SoG-Si production/MG-Si purification have been developed and upgraded by researchers for overcoming the low productivity of the Siemens process. These methods are classified into the following:

- thermal decomposition and/or H2 reduction of silane gases by improving the existing Si production methods that are based on the Siemens based processes;
- metallothermic reduction of Si halide compounds by Zn, Al and Na;
- upgrading metallurgical grade Si (MG-Si, 98–99% purity) via metallurgical (pyro- or hydro-) purification methods;
- fluoride processes for the preparation of high purity silicon; and
- reduction of silicon dioxide.
Due to high temperature demand of the conventional methods, Murray et al. (2006) presented a method that uses two-step solar process for the production of silicon from silica: a carbothermal reduction in the presence of nitrogen to yield silicon nitride and solar dissociation of the nitride to yield silicon. Braga et al. (2008) reviewed the advances made in silicon production and classified them as either chemical or metallurgical routes as shown in Fig. 16. Chemical methods (associated with the Siemens process) are exploited in companies such as Wacker Chemie AG, Tokuyama Corporation, Renewable Energy Corporation (REC) Group and Chisso Corporation while metallurgical routes (usually purification of metallurgical silicon) are employed in Solar Silicon Company (SOLSILC), Silicon Purification Technology (SPURT), Elkem, Kawasaki Steel Corporation, Apollon Solar and University of Campinas (UNICAMP). Both routes started with quartz with carbothermic reduction process to produce metallurgical silicon but with major differences at the purification stage where they acquire their appellations (chemical or metallurgical). In the chemical route, the low grade silicon is reacted with hydrochloric acid to form chlorosilanes that is then reduced with hydrogen gas to deposit a purer silicon grade while the metallurgical route uses fusion, refusion and solidification processes.

Gribov and Zinov’ev (2008) and Gribov and Zinov’ev (2003) present problems associated with polycrystalline silicon production for solar cells applications and highlighted new promising technologies. The criteria for the specification of SoG-Si that have been published by different authors differ in orders of magnitude and the origin of these values is not always clearly justified (Hofstetter et al., 2009). The acceptable contamination levels in solar grade silicon from feedstock to solar cell was modelled by Hofstetter et al. (2009) but the study is limited to Ti, Cr, Fe and Cu in a p-type mc-Si solar cell, in the initial mc-Si wafer and in the silicon feedstock. Investigations into amorphous-Si and the various degradations have been reported by researchers (Radue and Van Dyk, 2010; Tawada and Yamagishi, 2001; Yang et al., 2003). It has been revealed in the work and reviews of several researchers (Goetzberger and Hebling, 2000; Goetzberger et al., 2003; Lund et al., 2001; Carlson, 2003; Carlson and Wronski, 2003) that there is great hope for a-Si solar cells with subsequent reduction in the effect of the Staebler–Wronski effect.

Yasuda and Okabe (2010) reviewed the various methods employed in solar grade silicon production by metallothermic reduction in order to suggest inexpensive routes that suit industrial production to replace the expensive and low productivity Siemens-based processes. Arnberg et al. (2012) studied how demand for lower cost, better yield, higher efficiency and use of less pure silicon in solar cells are addressed by advanced solidification process.

4.3. Purification of silicon

Purification of silicon is an essential concept in industrial SoG-Si production since it is not generally produced directly without passing through a refining process. The earlier challenge of its production was due to shortage (Woditsch and Koch, 2002) of semiconductor grade which is expensive and off-spec (Morita and Yoshikawa, 2011). This later opened way for upgrading metallurgical grade silicon at lower cost though at the expense of loss of some silicon (Wei et al., 2011). Pizzini (2010) enumerated the challenges and benefits for low cost photovoltaic materials as regards solar grade silicon. Upgraded metallurgical grade silicon (UMG-Si) usually contains impurities that have been shown to greatly degrade photovoltaic performances such as the short-circuit current (JSC), open-circuit voltage (VOC), fill factor (FF) and power conversion efficiency (PCE) in silicon solar cells (Coletti et al., 2011; Davis et al., 1978, 1980).

Phosphorus diffusion gettering process has been widely used to improve the performance of Si solar cells in photovoltaic technology by improving the electrical properties of UMG-Si wafers and solar cells (Xu et al., 2010). In the study of Safarian et al. (2012),
the effect of impurities on PV module efficiencies and the impurity contents in silicon materials was reviewed. Lee et al. (2013) investigated the effects of metallic contaminant type and concentration (Al, Cu, Ni, and Fe) on the minority-carrier recombination lifetime and photovoltaic performance degradation of p-type silicon solar cells. The distributions of Al and Ca in mc-Si ingot (obtained from MG-Si) by vacuum induction melting and directional solidification processes were studied (Tan et al., 2014) and the results showed that at the initial stage of solidification, the impurity distribution is controlled by both segregation and evaporation while at the end stage, it is mainly determined by segregation due to the decrease of the diffusibility and evaporability with the decrease of melt temperature.

Several purification methods (Delannoy, 2012) had been investigated to get a stable SoG-Si and to reduce the production cost minimally without affecting the required properties of the built solar cells. It should be noted that most of these purification methods are simply preparation of SoG-Si from lower grades most especially MG-Si. It has been shown also that heat treatment could be used to modify the morphology of purified silicon. The effect of thermal annealing on the UMC-Si was investigated under different conditions by Wu et al. (2011). Thermodynamics of the various purification methods have been investigated by many researchers (Wu et al., 2013; Li and Guo, 2014; Ma et al., 2012; Morita and Miki, 2003) to have deep cognition of the processes.

Solvent refining process (Morita and Yoshikawa, 2011) is an important purification method that offers the possibility of cost reduction due to its high purification efficiency and low processing temperature. It involves alloying silicon with another element to enable the solvation and solidification with recrystallization of silicon from the solvent at a lower temperature than the melting point of silicon which is then followed by separation of the crystalized silicon. Yoshikawa and Morita (2012) reviewed solvent refining processes for SoG-Si purification with emphasis on their advantages and identifying the problems that must be solved for process development.

In general, several refining methods have been researched to include directional solidification (Martorano et al., 2011; Liu et al., 2012; Yoshikawa and Morita, 2009), fractional melting (Lee et al., 2009), leaching (Sahu and Asselin, 2012; Lian et al., 1992; Juneja and Mukherjee, 1986; Dietl, 1983; Zhanliang et al., 2011; Santos et al., 1990), slag treatment/gas blowing (Wu et al., 2013; Johnston and Barati, 2013, 2010; Jung et al., 2011; Cai et al., 2011; Li et al., 2013), electron beam melting (Pires et al., 2005; Liu et al., 2012; Sun et al., 2013; Peng et al., 2011), gravity separation (Li et al., 2012; Mitrašinović and Utigard, 2009), electromagnetic induction slag melting (Luo et al., 2011), vapourization (Morito et al., 2012; Zheng et al., 2011), zone refining (Mei et al., 2012), plasma refining (Wang et al., 2012; Delannoy et al., 2002; Degoulange et al., 2008; Zhao et al., 2011), concentrated solar radiation (Flamant et al., 2006), powder metallurgy technique (Gu et al., 2011) and integrated methods (Khattak et al., 2001; Hu et al., 2013; Schutz-Kuchly et al., 2011; Liang et al., 2010; Yuge et al., 2001, 1994; Mukashev et al., 2009; Martens et al., 2013; Visnovec et al., 2013) that use two or more of those aforementioned studies.

Fig. 16. Stages of the production of solar cells and panels that require research in the area of environmental control (Braga et al., 2008).
4.4. Silicon nanoparticles

Silicon nanoparticles have been prepared by many methods, such as fracturing porous silicon by ultrasonication (Belomoin et al., 2002), microwave-induced or laser-induced decomposition of silane (SiH₄)-like precursors (Holmes et al., 2001; Jones, 1996), low-temperature solution route (Neiner et al., 2006), low pressure chemical vapour deposition (Nakajima et al., 1996; Griskey, 1995), plasma-enhanced chemical vapour deposition (Mercaldo et al., 2009; Pi et al., 2006; Jawaid et al., 2012; Gabriel et al., 2010; Eng-Kwong et al., 2007), pulsed-laser ablation (PLA) of Si Gelloz et al., 2005; Shaaban et al., 2015, spark discharge (Tg, 2013) and electrolesso/ electrochemical etching (Bracmort, 2009; Nayfeh et al., 2003). The review of Ma et al. (2006) has dissected the various methods of preparation of silicon nanoparticles with their astonishing properties and applications. Solar-grade silicon microparticles were prepared by a two-stage technique consisting of a combustion process (metallothermic process) in a SiO₂ + Mg → Si + MgO reaction in an inert atmosphere and the hydrometallurgical treatment of the combustion product (Won et al., 2011), Su et al. (2012) directly prepared a low cost solar-grade mc-Si in a vacuum-diffusion solidification process starting with a 99.5% commercial metallurgical grade. Yasuda et al. (2011) investigated the production of solar-grade silicon by halothermic reduction of silicon tetrachloride (SiCl₄) based on the subhalide (SiO₂) reaction. The production of enhanced MG silicon for use in land-based solar cells could be synthesized from sodium silicate (Sudirmana et al., 2006 and several agricultural wastes (Zemnukhova et al., 2012; Ma et al., 2013; Rafiee et al., 2012; Carmona et al., 2013; Ogunfowokan et al., 2011, 2012; Mohanraj et al., 2012; Tang and Wang, 2005; Espindola-Gonzalez et al., 2010; Umeda and Kondoh, 2008; Yalcin and Sevinc, 2001; Oghenevweta et al., 2016; Özdemir and Yakuphanoglu, 2006; Ozin et al., 2008; Palmero et al., 2011; Pandey et al., 2009; Pokropivny et al., 2007; Yang et al., 2007; Zaluzev). Silicon is usually prepared by reflux technique of the extracted silica with 6.0 M HCl for 4 h and then washed repeatedly using distilled water. This was separated by centrifugation at 2500 rpm for 15 min and washing was repeated several times to remove impurities. The gel was later dried at 70 °C for 12 h and then sintered at 650 °C to yield silica nanopowder. Rafiee et al. (2012) also produced nanosilica from rice husk. Acid treatment of the rice husk was followed by thermal combustion under controlled conditions to give 22.50% ash with 90.469% silica. Nanosilica was prepared by reflux technique of the extracted silica with 6.0 M HCl for 4 h and then washed repeatedly using deionized water to make it acid free. It was then dissolved in 2.5 M sodium hydroxide by stirring. H₂SO₄ was titrated and precipitates started forming at pH > 10. The titration was stopped at three different pHs (1, 3 and 5) and the gel formed was washed with distilled water. This was separated by centrifugation at 2500 rpm for 15 min and washing was repeated several times to remove impurities. The gel was later dried at 70 °C for 48 h in the oven.

Espindola-Gonzalez et al. (2010) synthesized silica nanoparticles from rice husk, sugarcane bagasse and coffee husk by employing vermicompost with annelids (Eisenia fetida). The product (humus) was calcined at 500, 600 and 700 °C for 19 h and extracted with aqua regia to recover the crystalline nanoparticles. Another important source of silica that could be harnessed is the solid residues of the extracted silica. Zemnukhova et al. (2006) investigated and presented data on the purity (concentrations of metal oxides), morphology (particle size and shape), specific surface area, pore diameter, density, and water solubility of amorphous silica.

It is noteworthy that silica has been obtained by combination of processes such as acid treatment, partial burning (charring), burning, calcination, leaching, enzymatic treatment (Decker et al., 2007), pyrolysis, hydrolysis and sol-gel (Nayak and Bera, 2012;

\[
\text{SiO}_2 + X\text{SiC} \rightarrow \text{Si}_x\text{O}_y + \text{CO}
\]
Acid pre-treatment has been reported to improve the quantity and quality of the silica yield (Chandrasekhar et al., 2005; Chakraverty and Kaleemullah, 1991; Real et al., 1996). It was also reported to be very effective in removing metallic impurities, sulphur and phosphorus from the wastes (Rafiee et al., 2012; Carmona et al., 2013; Yang et al., 2005; Zalupec; Chakraverty and Kaleemullah, 1991; Chakraverty et al., 1988; Li et al., 2009; Krishnarao et al., 2001; Kalapathy et al., 2000; Zinin, 2011; Durowaye et al., 2014). This may be as a result of reaction between the metallic impurities with acid and similar process is repeated after calcination (Chakraverty and Kaleemullah, 1991). Several acids (mostly inorganic) have been employed to affect this phenomenon at low temperatures, usually below 110°C. Pre-burning is carried out at temperature below 500°C to reduce smoke formation and volume of dry matter prior to the burning of the agro-wastes which is between 550 and 800°C. Calcination is a process in which a material is heated to a temperature below its melting point to affect a thermal decomposition or a phase transition other than melting (McGraw-Hill, 2003). The temperature used depends on the materials being processed which could be as low as 400°C and above 1500°C. Pyrolysis is the thermochemical decomposition of organic material at high temperatures either in complete absence or limited supply of oxygen that gasification does not occur to an appreciable extent at temperature of between 500 and 800°C (Bridgewater and Bridge, 2002; Pande and Bhaskarwar, 2012). These processes are said to be controlled when the process is carried out in inert environment. Amorphous silica is formed at temperatures between 500 and 600°C but should always be kept below 700°C (Patel et al., 1987) to avoid the formation of crystalline forms, cristobalite and tridymite that are formed at 800 and 1150°C respectively (Vaibhav et al., 2015; Hamad and Khattab, 1981).

The entire thermal degradation takes place in three main stages of mass loss: drying, devolatilization and slow oxidation of fixed carbon (Chakraverty and Kaleemullah, 1991). This usually leads to the formation of silica ash, which could be white, brown, grey or black depending on inorganic impurities and unburnt carbon amount (Chakraverty and Kaleemullah, 1991; Chakraverty et al., 1988; Prasad and Pandey, 2012).

Leaching is dissolving soluble material from its mixture (usually solid) by a liquid solvent with an insoluble solid left. The solvent used may be acid or alkaline (McGraw-Hill, 2003). This is usually done to remove certain impurities present in the ash from which filtrate will be discarded or formation of a useful solution for further processing. Sol-gel method has been employed to obtain pure silica by dissolving an impure silica (usually ash) in an alkaline medium to form sodium silicate (Ogunfowokan et al., 2011; Tang and Wang, 2005; Palmero et al., 2011; Pokropivna et al., 2007; Yang et al., 2005; Vaibhav et al., 2015; Zemnukhova et al., 2006; Prasad and Pandey, 2012; Kamath and Proctor, 1998; Pijarn et al., 2010; Affandi et al., 2009; Okoronkwo et al., 2013). The dissolution of silica in NaOH by boiling at 100±10°C for 1 h with continuous stirring is according to Eq. (6) (Saravanan et al., 2012; Yuvakkumar et al., 2012).

\[
\text{SiO}_2(\text{impure}) + 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{SiO}_3(aq) + 2\text{H}_2\text{O}(l)
\]  

(6)

The solution will be filtered to separate undissolved contents while the filtrate is cooled to room temperature. The silica is then precipitated from the silicate by adjusting the pH slowly with acids to 7 or as low as 4 (for easier diffusion of sodium ions from the gel) and with constant stirring according to Eqs. (7) and (8) (Saravanan et al., 2012; Yuvakkumar et al., 2012).

\[
\text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{SiO}_2(\text{gel}) + \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l)
\]

(7)

\[
\text{Na}_2\text{SiO}_3(aq) + 2\text{HCl}(aq) \rightarrow \text{SiO}_2(\text{gel}) + 2\text{NaCl}(aq) + \text{H}_2\text{O}(l)
\]

(8)

Gelation starts immediately but this must be allowed to stay for about 18 h for complete ageing process. The formation of a sol-gel porous material is through a hydrolysispolycondensation reaction (Rappport and Apeloig, 1998). Effect of ageing time and concentration of ageing solution on the porosity characteristics of subcritically dried silica aerogels was studied by Smitha et al. (2006). The gel is then centrifuge to separate the silica from the mixture and thereafter dried. Estella et al. (2007) studied the effects of ageing and drying conditions on the structural and textural properties of silica gels.

### 5.2. Silicon

Larbi et al. (2012) produced silicon from RHA using both pyrometallurgical and hydrometallurgical processes. The RHA was leached with HCl and roasted in air before reduction by magnesium and finally recovered silicon through two steps of leaching with HCl and acetic acid at 150°C for 1 h. The silicon produced has an overall purity of over 99.3% with major impurities (<0.7%) being those metals that are more reactive than silicon.

Ikrak and Akhter (1988) prepared polycrystalline silicon by metallocthermic reduction of rice husk ash (RHA) which was obtained by leaching rice husk with HCl prior to burning in air to obtain a black ash. This was pyrolysed in a muffle furnace (in an alumina crucible) at 1070°C to obtain a white ash. The white ash was then leached with dilute HCl at 100°C to remove soluble impurities, rinsed with water, dried and ground into a very fine powder. The powdered white ash was reduced with magnesium at 620°C in a muffle furnace to obtain silicon with magnesium oxide and magnesium orthosilicate [2(MgO·SiO₂·O₄)·SiO₂] as the major impurities which are soluble in acids. The purity of silicon obtained was 99.95% after leaching with HCl.

Mishra et al. (1985) prepared a polycrystalline silicon of reasonable purity by metallocthermic reduction of purified rice husk white ash (amorphous silica) with calcium. High-grade amorphous silica was obtained from complete combustion of the rice husk at a temperature of 500°C. A silicon grade of 99.9% was obtained after leaching the reduced silica with concentrated HNO₃ and HF, as revealed by X-ray diffraction, SEM and emission spectrographic studies.

Banerjee et al. (1982) produced silicon from rice husks by metallocthermic reduction. Washed rice husk was sun-dried and then combusted in an electric furnace to give white ash. This was dissolved successively by dilute and concentrated HCl for 3–4 h and then washed and dried to determine the percentage of silica present. The dried ash was ground well, intimately mixed with magnesium (magnesium oxide powder was added to reduce the rate of reaction) to prepare a homogeneous mixture which was fired at different temperatures for about 1 h. The products were ground thoroughly before leaching with concentrated HCl (to remove MgO and other soluble impurities) for about 2 h. The products were then leached in a mixture of concentrated H₂SO₄ and HF at 110°C in a Teflon vessel for another 2 h, and the final residue was washed and dried.

Nandi et al. (1991) prepared hydrogenated amorphous silicon (a-Si:H) at a temperature of 460°C by thermal chemical vapour deposition (CVD) of silanes, generated by acid hydrolysis of magnesium silicide obtained from rice husk. White ash was obtained by burning rice husk in an electrical furnace under controlled supply of air at a temperature of 450±10°C. The white ash was then leached in different concentrations of HCl in a conventional Soxhlet apparatus to remove volatile and acid soluble impurities. The pure...
silica obtained was mixed with metallic magnesium powder and ignited under an inert atmospheric condition to convert it to magnesium silicide (Mg2Si). Silane gas mixtures (monosilane and disilane) were produced by reacting Mg2Si with dilute (10% by volume) hydrochloric acid before depositing the gas mixtures as a-Si:H thin films by thermal CVD technique on various substrates at a temperature of 460 °C under hydrogen atmosphere.

Venkateswaran et al. (2012) prepared solar grade silicon nanoparticles using nanosilica precursor (sol-gelled at pH of 5) prepared from rice husk with high temperature magnesiothermic reduction at different temperatures. 0.65 g of magnesium power was mixed with 2.0 g of aqueous gelatin solution (0.5 wt.%) containing dispersed 0.2 g of silica, and the mixture (ratio of SiO2:Mg is 1:2) was immediately freeze and lyophilized overnight. The obtained powder was heated in alumina crucible in a tube furnace for 5 h at 550, 650, 750 and 850 °C under nitrogen atmosphere. The obtained powder was washed 3 times and dried overnight at 60 °C to obtain silicon nanopowder. Sample prepared at 850 °C (98.20% purity) gave the best absorption of solar grade with an efficiency of 2.67%.

6. Conclusion

The challenges of electricity production in Nigeria are as aged as its independence with citizens’ hope lost. To improvise for their energy needs, they resulted to complete utilization of fossil fuels which has adverse effect on our climate. With the countries agricultural potential, it is quite easy to generate huge amount of greenhouse gases considering the quantity of wastes generated from its various activities. Nevertheless, these agricultural wastes can be converted to valuable resource, silicon, which is important in the fabrication of solar cells required to tap into the Sun’s inexhaustible energy. This has the potential of generating green electricity for the populace and consequently reducing the menace of climate change that ever government of the world is seriously trying to halt. This review critically considers the potential of producing solar grade silicon from numerous agricultural wastes in Nigeria relying on the previous works executed by several researchers across the world. All the previous works concentrated on production of silicon from rice husks while other vast agricultural wastes of importance to Nigeria need to be investigated. The silicon nanoparticles obtained from this source can be dispersed in liquids for spin coating of substrates.

References
