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QUALITATIVE ANALYSIS OF HIGH GRADE NANOSILICON OBTAINED FROM COASTAL LANDFORM IN ESE ODO LOCAL GOVERNMENT AREA OF ONDO STATE, NIGERIA

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ABSTRACT

The research focused on the qualitative analysis of high grade nanosilicon obtained from coastal landform in Ese Odo Local Government Areas of Ondo State, Nigeria. The landform in the study areas were noted to possess different colours with appearances and physical presentation presumably of silicon content. The Silicon from the landform were obtained using magnesium as a reducing agent. The results of the energy dispersive x-ray (EDX) analyses of the samples ball-milled for 24 hours revealed that silicon has the highest percentage of all the elements observed in the spectra. The morphology of nanosilicon from Pekehan revealed the presence of agglomeration of irregular shaped particles with average particles sizes of 50.27 nm while Igbekebo and Oju-ala coastal landforms showed the presence of agglomerated ovoid shape with average particle sizes of 54.25 nm and 53.52 nm respectively. The X-ray Diffraction (XRD) spectral of the nanosilicon shows sharp distinct peaks which indicate crystalline nature of the samples. Based on the results obtained, it can be concluded that, the percentage of nanosilicon values obtained ranges between 68.85% to 73.03% which are relatively high enough and can find suitable industrial applications in sectors like the lithium-ion battery, biomedical devices, photovoltaic/solar cell and computer industries etc.

Keywords: Coastal landform, Ball-milling, Nanosilicon, Qualitative analysis

INTRODUCTION

Silicon is one of the best researched materials ever discovered by mankind and the semiconductor industry mostly uses silicon. The information technology revolution has been made possible by the discovery of silicon's properties. The developments in the vast area of nanotechnology have demonstrated that size reduction can be used to overcome the limits of bulk materials. When silicon is reduced to a size in the 1-100 nm range, quantum confinement has a significant impact on its properties and performance (Klaus, 2017). Research in electronics and photonics has revealed the peculiar properties of these materials, which have been used in biomedicine for tissue engineering, drug delivery, biosensing, radiotherapy, and sonodynamic therapy. This is possible because of the good biocompatibility and biodegradability of nanoscale silicon. Additionally, Si-based nanoparticles are being researched for application in optoelectronics (Sailor 2012), photovoltaics (Wu *et al*., 2001; Halbwax *et al.,* 2008), and sensorics (Lin *et al.*, 1997; Ahn *et al.,* 2013). The nanoparticles differ from the bulk state of a similar material due to their larger surface area that is easily available (Obinson, 2013). In comparison to the bulk, the surface of nanoparticles typically exhibits softer vibration modes and thermal characteristics which work at lower temperatures. The synthesis of silicon by thermal reduction has employed a variety of materials such as Rice husks (Liu *et al.,* 2013, Matsumoto *et al.,* 2018), diatoms (Bao *et al.,* 2007), land-based plants (batchelor *et al.,* 2012) (rice grasses, sugarcanes), bamboo (batchelor *et al.,* 2012, Kumar *et al.,* 2016), silicon monoxide (Gao *et al.,* 2017) and sand (Hai *et al.,* 2009, Furquan *et al.,* 2018). Sand is a naturally occurring, low-cost raw material. Magnesium is used as a reducing agent in the process of extracting silicon from sand.

Recent interest has been focused to magnesiothermic reduction due its noticeably lower working temperatures (650ºC) (Favors, *et al.,* 2014, Oluyamo, *et al*., 2023). The manufacture of silicon from sand by using magnesium as a reducing agent was primarily investigated as a potential anode material that might be used for rechargeable Lithium-ion batteries. (Hai *et al.,* 2009, Favors *et al.,* 2014; Yoo *et al.,* 2014 and Arunmetha *et al.,* 2018). Solar cell fabrication is another potential use of silicon (Arunmetha *et al.,* 2018 and Venkateswaran *et al.,* 2013). Similarly, luminous silicon nanoparticles were produced by reducing silica particles using a magnesiothermal (Matsumoto *et al.,* 2018, Zhu *et al.,* 2010 and Chen *et al.,* 2012). There are many ways of producing nanosilicon, including using sol gel, vapour phase, the thermal decomposition technique, thermal pyrolysis, chemical precipitation, electrospinning, lithography and biotransformation. Chemical treatment uses the acid and base solution method, but this procedure is costly, complex, and uses a lot of energy. Because of this, it is essential to use versatility and unique methods to produce silicon nanoparticles. The balling method has numerous advantages over other processes, including efficiency, high product purity, moderate reaction temperature, controllability, simplicity, and reproducibility.

By reducing silicon to the nanoscale, it can adequately accept strain and avoid fracture (Chan *et al.,* 2008, Wu *et al.,* 2012, Liu *et al.,* 2012, Wu and Cui, 2012). Several studies have been conducted on the extraction of elemental silicon using various starting materials, such as rice husk, sugarcane bagasse, corn cob, however there is little or no precise information on the isolation of nanosilicon from any of these materials. It is interesting to note that the landform in the studied areas have different colours and are merely utilized for agriculture. In addition to the possibility that the sand contain high grade silicon, the colour of the landforms is thought to have an influenced on silicon contents. In another way, it is believed that research on the qualitative analysis of nanosilicon will raise the landforms' industrial value.
The study will provide a source of high grade silicon and nanosilicon for industrial uses and act as a data base for the

creation of new strategies for transforming landforms into applications that are productive.
The aims of the study is to investigate the qualitative analysis of high grade nanosilicon obtained from the coastal landform. Then the qualitative analysis was conducted using energy dispersive x-ray (EDX), scanning electron microscopy (SEM) and x-ray diffraction (XRD).

MATERIALS AND EXPERIMENTAL METHOD

Materials

The sand used in this research work were from the coastal landform from Ese-Odo Local Government Area of Ondo State, Nigeria. Hydrochloric acid (HCl) (36%), sodium hydroxide (NaOH) and magnesium powder (Mg) were purchased from Pascal Scientific Ltd and used as analytical chemical reagents. Distilled water was used in the preparation of all solutions. Ball milling is a mechanical technique used to grind the materials into nanoparticles.

Collection of samples

The samples were collected into non-reacting polyethylene bags at a depth approximately about 30 cm below the surface. The locations of the areas where the samples were taken along with their sources are shown in Table 1.

Samples preparation

50 grams of each sand sample were successively washed for 3 hours in 250 ml of 1 M hydrochloric acid (HCl) at 75 ºC and 1M sodium hydroxide (NaOH) at room temperature. After each process, distilled water was used to wash away any remaining acid or alkali traces. The washed sand sample was oven dried for a period of 2 hours at 105 ºC. The sand samples were sieved into 63 µm using a mechanical test sieve shaker to ensure a homogenous size distribution and enhance purity of the materials.

Table 1: Location/sources Covered with their Position Using Global Positioning System (GPS)

Coastal Landforms	Sources	Colour	Physical Texture	Longitude (ºE)	Latitude (ºN)
Pekehan	Pekehan Seaside, Igbekebo, Ese Odo LGA	White	Smooth	004.86137	06.35244
Igbekebo	Igbekebo, Agbala Road, White Sand Zion, Ese Odo LGA	White	Smooth	004.86287	06.35091
Oju-Ala	Oju-Ala Igbotu, Ese Odo LGA	Redish Brown	Smooth	004.88792	06.40769

Silica reduction with magnesium and synthesis of nanosilicon

To ensure effective reaction, 16.0 g of silica sand and 15.0 g of magnesium powder (180 µm) were thoroughly mixed together. This was then put into a crucible and heated for 30 minutes at 800 ºC (Onojah *et al.,* 2012; Vazeed *et al.*, 2015 and Oluyamo *et al*., 2023). The samples were then allowed to gradually cool to room temperature. The reaction's equation is as follows:

SiO_2 (s) + 2Mg (s) 2MgO (s) + Si (s) (1)

MgO and Si are formed when silica and magnesium powder are heated. One gram (1 g) of silicon (Si) sample is washed in 20 ml of 5 M HCl at 100 ºC and stirred with a magnetic stirrer for 60 minute for effective leaching to occur, the unreacted Mg and its products are entirely removed. Distilled water was thoroughly used to wash the product that had been leached by hydrochloric acid. The washed silicon (Si) samples are then dried for 5 hours at 105 ºC in an oven before being stored in a desiccator. High energy ball- mill was used to grind dried silicon particles into nanoparticles. With the aid of EDX, SEM (using JOEL-JSM 7600F NanoSEM equipment) and XRD (using GBC EMMA XRD equipment, Australia), the isolated nanosilicon was analysed.

Theoretical Background

The Bragg Equation (2) was used to calculate the interplanar spacing or d-spacing (Wada and Okano, 2001; Kim, *et al*., 2010; Oluyamo, *et al*., 2023).

$$n\lambda = 2d sin\theta \qquad (2)$$

where n denotes order of reflection, λ denotes wavelength of the incident X-ray (m), d denotes interplanar spacing of the crystal, and θ denotes Bragg's angle (º).
Using Scherrer's equation, the crystallite size (L) was determined. It is given as:

$$L = \frac{K\lambda}{BCos\theta} \qquad (3)$$

where K is a constant value given as 0.91, λ is the incident X-rays' wavelength, θ is the Bragg's angle, B is the intensity of the full width at half maximum (FWHM).

RESULTS AND DISCUSSION

Energy Dispersive X-ray (EDX) Analysis

Energy dispersive x-ray (EDX) analysis was used for determining the elemental composition of the raw samples from the coastal landform as indicated in Table 2. In terms of the elements observed in the spectra, EDX indicates that silicon has the highest percentage. Na, K, Al, and Fe impurities in quartz sands are assumed to originate from mica and feldspar minerals (Dal-Martello *et al*., 2011). For significant industrial use, the range of silicon content (i.e. 53.60 - 58.52) in the raw samples as collected from the relevant sources (i.e. Pekahan, Igbekebo, and Oju-ala landforms) is considered to be quite low.

Table 2: Results of the percentage of elements in the Landforms revealed by the EDX analysis.

Element	Coastal Landforms		
	Pekehan	Igbekebo	Oju-Ala
Si	58.52	54.70	53.60
Mg	1.30	3.40	0.37
C	3.24	3.00	4.20
O	14.20	14.60	16.30
Ca	4.22	9.00	3.30

Fe	5.70	2.60	8.50
S	-	-	-
Na	2.40	0.20	3.22
K	-	1.40	-
Al	10.30	10.00	10.40
Mn	0.10	1.10	0.11

Nevertheless, the energy dispersive x-ray (EDX) analyses after the process of isolation indicated that the nanosilicon obtained from the samples ranged between 68.85% to 73.03% as shown in Figures 1-3. Coastal landform obtained from igbekebo had the highest percentage while that obtained from Pekehan had the lowest percentage value of nanosilicon. This may be as a result of the samples' chemical composition as previously established by Victor and Alvaro (2015). The values are high enough to be beneficial in the manufacture of materials and industrial use. Although sulphur and potassium were not detected in the raw samples, their appearance in the obtained samples may have been introduced into the materials via the sample holder of the EDX equipment as well as the chemicals used in the preparation of the samples.

Scanning Electron Microscopy (SEM) Analysis

As presented in Figure 1- 3, the morphology of nanosilicon from Pekehan revealed the presence of agglomeration of irregular shaped particles with average particles sizes of 50.27 nm while Igbekebo and Oju-ala coastal landforms showed the presence of agglomerated ovoid shape with average particle sizes of 54.25 nm and 53.52 nm respectively. The result obtained showed that the high energy balling milling is effective for reducing the silicon into nanosize. The existence of agglomerates is an unavoidable phenomenon that is occur when small particles interact with one another due to electrostatic attraction or van der Waals force (Ruksudjarit & Rujijanagul, 2008). The small sizes of the nanosilicon obtained reveals that they can be effectively utilized for suitable application. The percentage values of the nanosilicon are also indications of possible attraction of the landforms for the production of high grade silicon materials for industrial applications and utilization which affirms findings in recent research by Oluyamo *et al*., 2023.

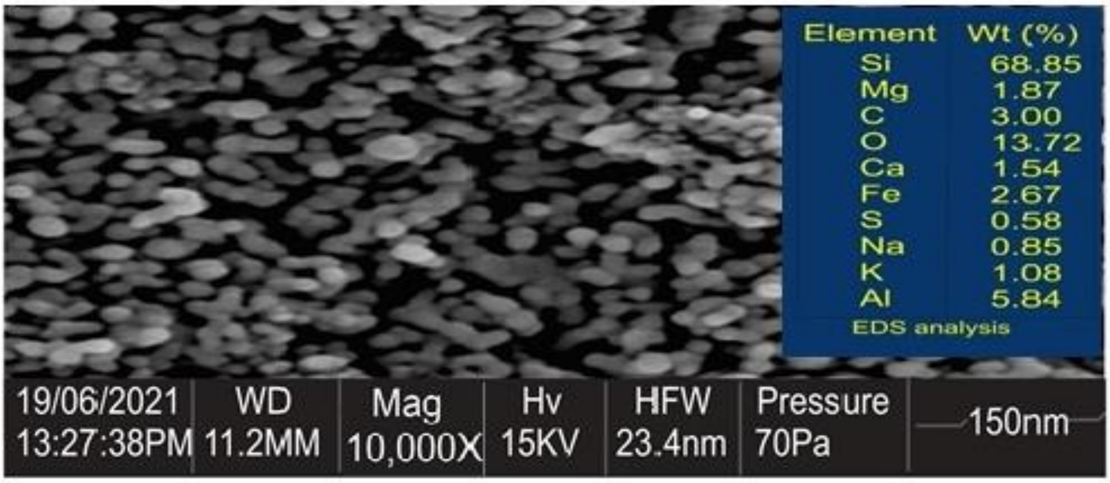

Figure 1: SEM image of nanosilicon of Pekehan coastal landform and the percentage elemental composition.

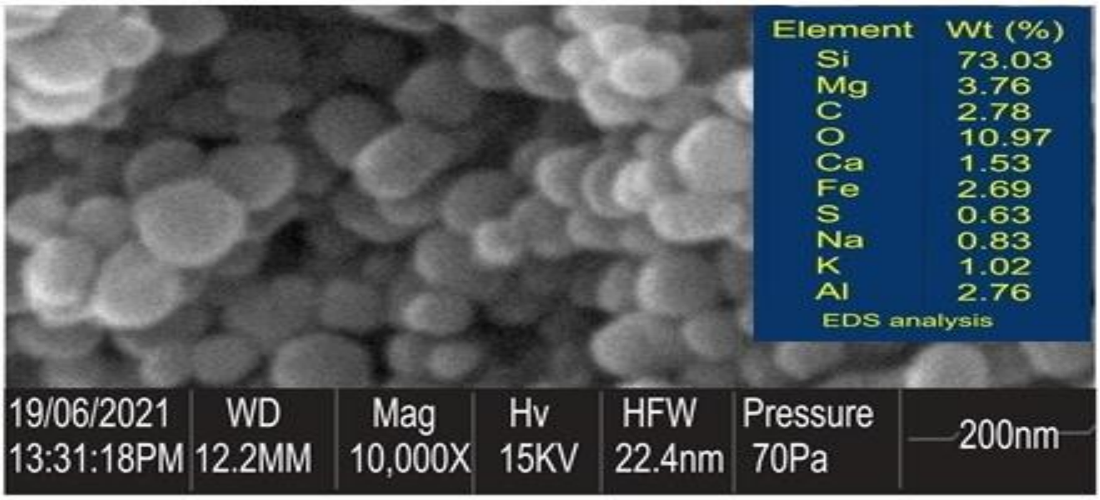

Figure 2: SEM image of nanosilicon of Igbekebo coastal landform and the percentage elemental composition.

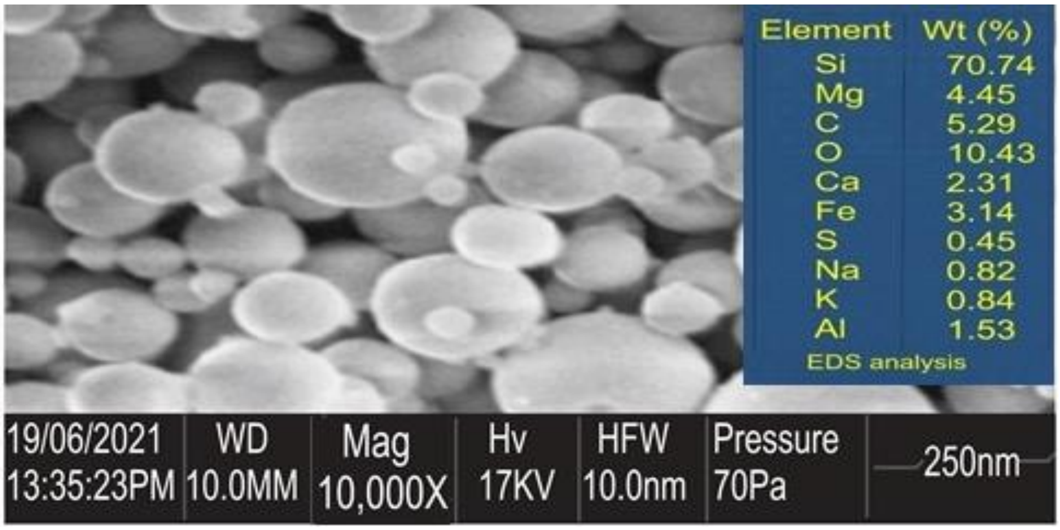

Figure 3: SEM image of nanosilicon of oju- ala coastal landform and the percentage elemental composition.

X-ray Diffraction (XRD) Analysis of Nanosilicon

Well-oriented and sharp distinct crystalline peaks were obtained in the X-ray diffraction patterns as shown in Figures 4-6. It was noticed that the silica had pronounced peak in the sample. This could be probably due to contact of the silicon powder with air especially during storage. Darghouth *et al.,* 2021 had also attributed the presence of oxygen to the excess of silica that was not removed via HCl leaching. The nanosilicon's band position (2θ), full width at half maximum (FWHM), crystallite size, and d-spacing are all presented in Table 3. Calculations using Scherrer's equation (3) showed that the crystallite sizes were 45.37 nm, 47.55 nm and 45.80 nm for Pekehan, Igbekebo and Oju-Ala coastal landforms, respectively. As shown in Table 3, X-ray diffraction patterns of the nanosilicon for the coastal landforms showed that the diffraction peak planes are in good agreement with the International Centre for Diffraction Data (ICDD).

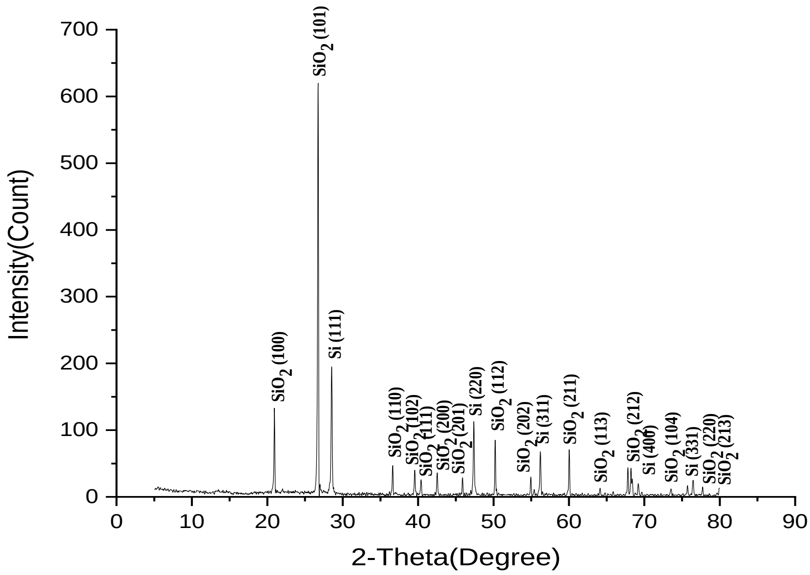

Figure 4: X-ray diffraction pattern of nanosilicon of Pekehan coastal landform

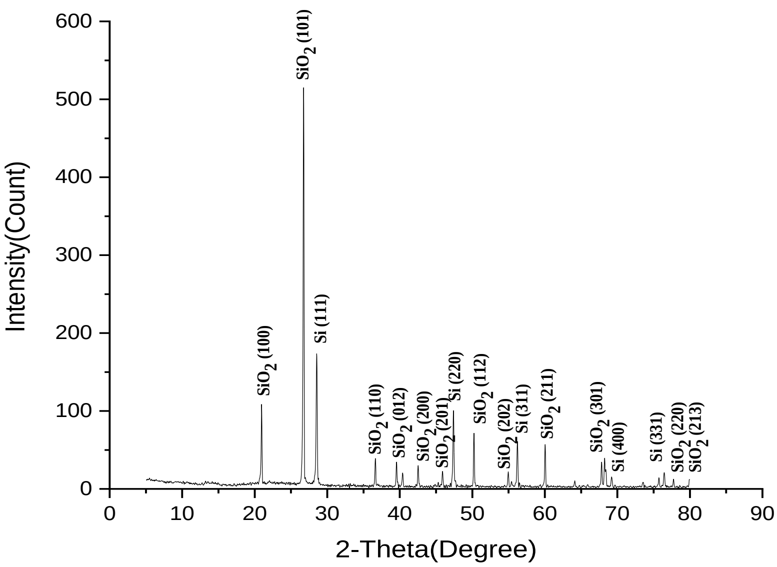

Figure 5: X-ray diffraction pattern of nanosilicon of Igbekebo coastal landform

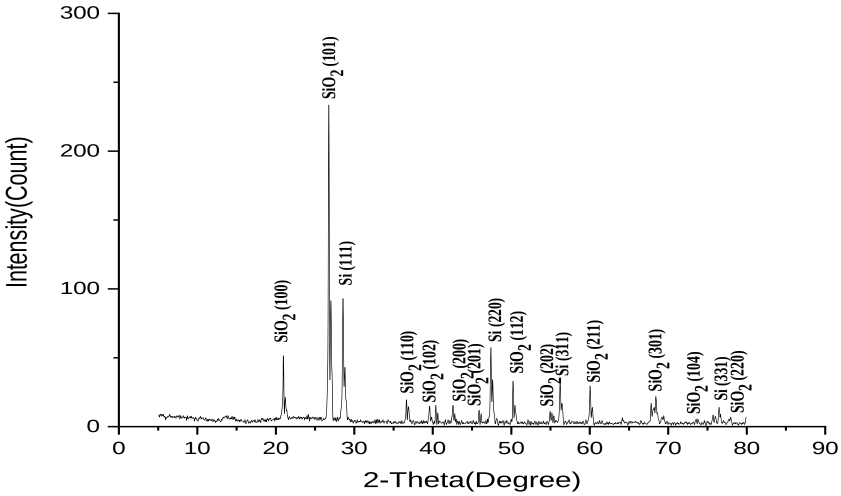

Figure 6: X-ray diffraction pattern of nanosilicon of Oju- ala coastal landform

Table 3: Band position (2θ), FWHM, Crystallite size and d-spacing of Nanosilicon

Coastal Landforms	2θ	FWHM (β) (rad)	Crystallite Size (nm)	D-Spacing d (A^0)	Ref. Code Marching (ICDD) Silicon	Synthesis Quartz (SiO_2)
Pekehan	28.54	0.003189	45.3689	3.122297	00-026-1481	00-033-1161
Igbekebo	28.56	0.003042	47.5543	3.135500	00-026-2656	01-083-2602
Oju-Ala	28.56	0.003159	45.7988	3.122750	00-027-2561	00-003-2407

CONCLUSION

The study examined the qualitative analysis of high grade nanosilicon obtained from Coastal Landform in Ese Odo Local Government Area of Ondo State, Nigeria. The result obtained from EDX and SEM revealed that quality nanosilicon were produced. The samples that were analysed revealed that silicon and oxygen were prominent. Consequently, the result of the research indicates that nanosilicon can be obtained from the silica sand found in the study area. In addition, the value of silicon are of high grade that makes it suitable for industrial applications and use in sectors including the lithium ion battery, biomedical devices, photovoltaic/solar cell and computer industries.

REFERENCES

Ahn, J. H., Kim, J. Y., Seol, M. L., Baek, D. J., Guo, Z., Kim, C. H., Choi, S. J. and Choi, Y. K. (2013). A pH sensor with a double-gate silicon nanowire field-effect transistor. Appl Phys Lett 102 (8): 083701

Arunmetha, S., Vinoth, M., Srither, S., Karthik, A., Sridharpanday, M., Suriyaprabha, R., Manivasakan, P. and Rajendran, V. (2018). Study on production of silicon nanoparticles from quartz sand for hybrid solar cell applications. Journal of Electron Materials 47 (1): 493–502

Bao, Z., Ernst, E. M., Yoo, S. and Sandhage, K. H. (2009). Syntheses of porous self-supporting metal-nanoparticle assemblies with 3D morphologies inherited from biosilica templates (diatom frustules). Advance Materials 21 (4): 474–478

Bao, Z., Weatherspoon, M. R., Shian, S., Cai, Y., Graham, P. D., Allan S. M., Ahmad, G. and Dickerson, M. B., Church, B. C., Kang, Z., Abernathy, H. W., Summers, C. J., Liu, M and Sandhage, K. H. (2007). Chemical reduction of three-dimensional silica micro- assemblies into microporous silicon replicas. Nature 446 (7132): 172–175

Batchelor, L., Loni, A., Canham, L. T., Hasan, M. and Coffer, J. L. (2012). Manufacture of mesoporous silicon from living plants and agricultural waste: an environmentally friendly and scalable process. Silicon 4 (4): 259–266

Chan, C. K., Peng, H., Liu, G., McIlwrath, K., Zhang, X. F., Huggins, R. A. and Cui, Y. (2008). High-performance lithium battery anodes using siliconnanowires. Nature nanotechnology 3, 31-35.

Chen, K, Bao, Z., Shen, J., Wu, G., Zhou, B. and Sandhage, K. H. (2012). Freestanding Monolithic silicon aerogels. Journal of Materials Chemistry 22 (32): 16196-16200

Cui, L. F., Hu, L., Wu, H., Choi, J. W. and Cui, Y. (2011). Designing nanostructured Si anodes for high energy lithium ion batteries. Journal of The Electrochemical Society 158, A592.

Dal Martello, G., Tranell, E., Gaal, S. Raaness, O. S, Tang, K. and Arnberg, L. (2011*). Study* of Pellets and Lumps as Raw Materials in Silicon Production from Quartz and Silicon Carbide, Metallurgical and Materials Transactions B, Volume 42b, 939-950

Darghouth, A., Aouida, S. and Bessais, B. (2021). High Purity Porous Silicon Powder Synthesis by Magnesiothermic Reduction of Tunisian Silica Sand. Silicon 13 (7): 667

Favors, Z., Wang, W., Bay, H. H., Mutlu, Z., Ahmed, K., Liu, C., Ozkan, M and Ozkan, C. S. (2014) Scalable synthesis of nano-silicon from beach sand for long cycle life Li-ion batteries. Sci Rep 4: 5623

Furquan, M., Khatribail, A. R., Vijayalakshmi, S. and Mitra, S. (2018). Efficient conversion of sand to nano-silicon and its energetic Si-C composite anode design for high volumetric capacity lithium-ion battery. J Power Sources 382: 56–68

Gao, P., Tang, H., Xing, A. and Bao, Z. (2017). Porous silicon from the magnesiothermic reaction as a high-performance anode material for lithium ion battery applications. Electrochim Acta 228: 545–552

Hai, N. H., Grigoriants, I. and Gedanken, A. (2009). Converting Stöber silica and Mediterranean sand to high surface area silicon by a reaction under autogenic pressure at elevate temperatures. Journal of Physical Chemistry C 113 (24): 10521–10526

Halbwax, M., Sarnet ,T., Delaporte, P., Sentis, M., Etienne, H., Torregrosa, F., Vervisch, V., Perichaud, I. and Martinuzzi, S. (2008). Micro and nano-structuration of silicon by femtosecond laser: application to silicon photovoltaic cells fabrication. Thin Solid Films 516 (20): 6791–6795

Hertzberg, B., Alexeev, A. and Yushin, G. (2010). Deformations in Si−Li Anodes Upon Electrochemical Alloying in Nano-Confined Space. Journal of the American chemical society 132: 8548

Kim, U. J., Eom, S. H. and Wada, M. (2010). Thermal decomposition of native cellulose: Influence on crystallite size, Polymer Degradation and Stability 95, 778- 781

Klaus, D. S. (2017). Silicon nanomaterials source book low-dimensional structures, quantum dots, and nanowires. CRC Press Taylor and Francis Group 1: 1-643

Kruis, F. E., Goossens, A. and Fissan, H. (1996). Synthesis of semiconducting nanoparticles. Journal of Aerosol Sci 27: 165–166

Kumar,V., Tiwari, P., Krishnia, L., Kumari, R., Singh, A., Ghosh, A and Tyagi, P. K. (2016). Green route synthesis of silicon/silicon oxide from bamboo. Advanced Materials Letter 7: 271–276

Lin, V.S. Y., Motesharei, K., Dancil, K. P. S., Sailor, M. J. and Ghadiri, M. R. (1997). A Porous silicon-based optical interferometric biosensor. Science 278 (5339): 840–843

Liu, N., Huo, K., McDowell, M. T., Zhao, J. and Cui, Y. (2013). Rice husks as a sustainable source of nanostructured silicon for high performance Li-ion battery anodes. Sci Rep 3: 1919

Liu, S., Liu, B., Yao, Y., Dong, P. and Zhao, S. (2016). Effect of pore structures on the electrochemical performance of porous silicon synthesized from magnesiothermic reduction of biosilica. Journal of Wuhan Univ Technol Mat Sci Ed 31 (5): 965–971

Liu, X. H., Zhang, L., Mao, S. X., Zhu, T. and Huang, J. Y. (20120. Size-Dependent Fracture of Silicon Nanoparticles During Lithiation. American Chemical Society Nano 6 (2): 1522- 1531

Matsumoto, K., Kamiya, K., Ito, S., Kawabata, S. and Inada, M. (2018). Luminescent Si nanomaterials prepared from rice husks of agricultural waste. Trans Mat Res Soc Japan 43 (3): 167–170

Oluyamo, S. S., Famutimi, O. F. and Olasoji, M. O. (2023). Isolation and Characterisation of High Grade Nanosilicon from Coastal Landform in Ilaje Local Government Area of Ondo State, Nigeria. African Scientific Report, 2 (1), 82

Onajah, A., Amah, A. N. and Ayomanor (2012). Comparative studies of silicon from rice husk ash and natural quartz. American Journal of Scientific and Industrial Research, ISSN: 2153 649X, 3 (3): 146-149

Robinson, I. (2013). Nanoparticle Structure by Coherent X-ray Diffraction. Journal of the Physical Society of Japan, 82 (2) : 1-19. Article 021012. DOI: 10.7566/JPSJ.82.021012

Ruksudjarit, A. and Rujijanagul, G. (2008). Synthesis of SiO2 nanopowder from rice husk Ash. Advanced Materials Research 55, 649.

Sailor, M. J. (2012). Porous silicon in practice: preparation, characterization and applications. John Wiley & Sons, Science - 262 pages.

Vazeed, M. D., Akash, J., Anusha, M. and Ajay, K. V. (2015). Quantitative and Qualitative Analysis of Silicon extracted from Godavari river sand, Kandakurthi, Telangana, India International Journal of Engineering Research & Technology (IJERT) 4 (11): 2278-0181

Venkateswaran, S., Yuvakkumar, R. and Rajendran, V. (2013). Nano silicon from nano silica using natural resource (RHA) for solar cell fabrication. Phosphorus Sulfur Silicon Relat Elem 188 (9): 1178– 1193

Victor, C. and Alvaro, R. (2015). Measure of the colour of beach nourishment sands: A case Study from Belgium coast, Article in Trabajos de Geologia, Universidad de Oviedo, 35: 7-18

Wada, M. and Okano, T. (2001). Localization of Iα and Iβ phases in algal cellulose revealed by acid treatments, Celluolose, 8 (3), 183-188

Wu, C., Crouch, C. H., Zhao, L., Carey, J. E., Younkin, R., Levinson, J. A., Mazur, E., Farrell, R. M., Gothoskar, P. and Karger, A. (2001). Nearunity below-band-gap absorption by microstructured silicon. Appl Phys Lett 78 (13): 1850–1852

Wu, H., Chan, G., Choi, J. W., Ryu, I., Yao, Y., McDowell, M. T., Lee, S. W., Jackson, A., Yang, Y., Hu, L. and Cui, Y. (2012). Stable cycling of double-walled silicon nanotube battery anodes Through solid-electrolyte interphase control, Nat. Nanotechnol. 7, 310- 315

Wu, H. and Cui, Y. (2012). Designing nanostructured Si anodes for high energy lithium ion batteries. Nano Today 7 (5): 414-429

Yoo, J. K., Kim, J., Choi, M. J., Park, Y. U., Hong, J., Baek, K. M., Kang, K. and Jung, Y. S. (2014). Extremely high yield conversion from low-cost sand to high-capacity Si electrodes for Li-ion batteries. Adv Energy Mater 4 (16): 1400622

Zhu, J., Wu, J., Wang, Y. and Meng, C. (2010). Synthesis and characterization of mesoporous silicon directly from pure silica sodalite single crystal. Journal of Material Science 45 (24): 6769–6774