Low-cost green Synthesis of Silica Engineering Nanomaterials from rice husk (Agriculture waste) and its physical and luminescent properties measurements

Akansha Kumari, Rakesh Kr Singh*, Abhay Kr Aman, Nishant Kr, Ajitendra Kr Singh

Aryabhatta Center for Nanoscience and Technology, Aryabhatta Knowledge University, Patna, India

*Corresponding author email: rakeshsinghpu@gmail.com

Abstract: The electrical, electronics, and drug industries are heavily reliant on the use of Silica materials for several applications. Green source of production of silica materials is very important to meet the growing demand for industrial purposes. The present work discusses the recent nanosilica production using low-cost methods, from rice husk-agricultural waste, and their structural, microstructural, and optical properties measurement for its applications. The crystallite size of silica particles was measured using XRD is 26 nm and 55 nm, which are prepared from rice husk synthesized by both coprecipitation and leaching processes, respectively.. The SEM images of both the samples showed structural order of the pores within the mesoporous structure. The leached sample showed a purity of around 80%. The infrared spectral data also supports the presence of hydrogen-bonded silanol groups and the siloxane groups in the silica. These nanosilica particles showed Photoluminescence in UV, Visible, and NIR regions. The nanoscale silica formation is also confirmed by TEM and DLS measurements. Zeta Potential studies found -22.12 mV reveals the stability of prepared nano silica for a longer duration.

1. Introduction: Nationwide concerns of energy-related climate change linked with the spiralling cost of fossil fuels have increased interest in renewable energy sources as an alternative source. During the last about 25 years, human activities such as the production and consumption of fossil fuels as well as agricultural and industrial activities have caused an increase in the atmospheric concentration of greenhouse gases [1]. The rice husk is not suitable for human consumption. The disposal of the ashes and partially bored husk creates environmental hazards. One interesting application of rice husk is the production of silica nanoparticles at low cost and high efficiency [2]. Silica has been used for gene delivery to obtain more efficient DNA delivery vectors for both basic research and clinical trials in medical sciences [3]. It generally contains about 75% of the organic matter that evaporates while burning of husk and the rest obtained is rice husk ash and contains 85-90% amorphous silica, is highly porous and lightweight with very high external surface area. Its absorbent and insulating properties are useful for acting as a strengthening agent in building materials, Drug delivery, etc. [4-5]. Silica naturally exists in the form of nanoparticles in rice Husk. It accumulates around cellulose micro-compartments. When as a living thing (plant state) rice absorbs silica in the form of silicic acid from the soil and the silica accumulates around cellulose micro-compartments. When burnt rice husk (RH) gives rice husk ash (RHA)

which is a potential source of reactive amorphous silica. Silicon is the second most abundant element on the earth's crust. Moreover, it is considered an essential nutrient for plants and beneficial for crops like rice, wheat, etc. Rice plant absorbs silicon through the soil. That accumulates in the micro cellulose compartments of the grain cover. Silicon is not very reactive although more reactive than carbon. It readily reacts with oxygen. Materials with porous features on the nanoscale have important applications in optics, catalysis, drug delivery systems, hydroelectric cell, coatings, cosmetics, bio-separation, diagnostics, gas separation, and nanotechnology [6-10]. Nanoporous materials consist of an amorphous or crystalline framework with void spaces, which may be cylindrical or cage-like. Porous silica in nanophase possesses a high density of surface silanol (Si-OH) groups after calcination. The reactions of these silanols with various silanes produce different functional groups on the silica framework, which helps in the conjugation of molecules. The objective of the present research is to prepare a technological-grade nanomaterial from agricultural waste. Further, the material prepared should be porous which may be used in varied applications.

2. Materials and Methods:

Synthesis of nano silica from agriculture waste-rice husk: In the present work, the main objective was to obtain crystalline nanosilica of high purity as functional nanomaterial. Two different synthesis techniques were used to prepare two different samples and their properties were compared. The samples were prepared using Rice Husk Ash (RHA). In the first process, the Rice Husks were burnt in the open air and then the ash was further burnt in the high-temperature furnace at 800°C for 3 hours at a ramp rate of 6°C/min. Then the base treatment was done using 2.5 N NaOH. Then it was treated with conc. H_2SO_4 to maintain pH 2, adding liquid ammonia drop by drop to shift the solution to pH value 9. The produced Silica is then treated with 6N HCl. The procedure was then followed by base treatment (2N NaOH). Then pH was adjusted to 8.5 by adding sulphuric acid. With the pH shift the solution starts to participate. This indicates the formation of nanosilica. In the second process, the Rice Husk was burnt in the high-temperature furnace at a temperature 800°C for 3 hours (6°C/min). The ash obtained was leached in HCl acid for 2 hours. The filtered and dried RHA was again heated in a high-temperature furnace at a temperature of 700°C for 3 hours (6°C/min). The flow chart for the preparation of Nano silica from rice husk as a schematic diagram is shown in figure-1. The RHA was then treated with base NaOH. The solution was kept in a hot air oven for an hour. The precipitate was obtained which was oven-dried for half an hour. Then it was treated with acid (HCl). The solution was kept in the ice bath for an hour. The filtered solution was oven-dried for 24 hours. The nano silica by both processes obtained was then characterized using characterization tools XRD, TGA & DTA, SEM, FTIR, Zeta potential, and PL.

3. Results and discussion

3.1. TGA-DTA measurement: Both Biological and inorganic components make up rice husk. At high temperatures, each of these chemicals exhibits a distinct behaviour. Thermogravimetric analysis (TGA), which is regarded as a crucial instrument for the identification and characterization of materials, can be used to observe this behaviour. The TGA curve in figure-2 demonstrated the weight changes that happened when the rice burned. The matching derivative profile of the DTA, which indicates the rate at which mass loss changes with temperature, is displayed in the insert of this figure-2. The TGA curve demonstrated the weight changes that happened when the rice burned. The matching derivative profile of the thermal analysis, which indicates the rate at which mass loss changes with temperature, is displayed. Based on the peaks related to the mass changes, the thermal analysis

was divided into three stages: stage 1, which was found to be between room temperature and 140°C; stage 2, which was found to be between 150 and 350°C; and stage 3, which was found to be between 350 and 500°C. The breakdown of

3.2. Structural analysis using XRD Measurement: Two Nano silica samples as a SiO_2 from rice husk were prepared by two different methods, sample 1 (raw RHA) and
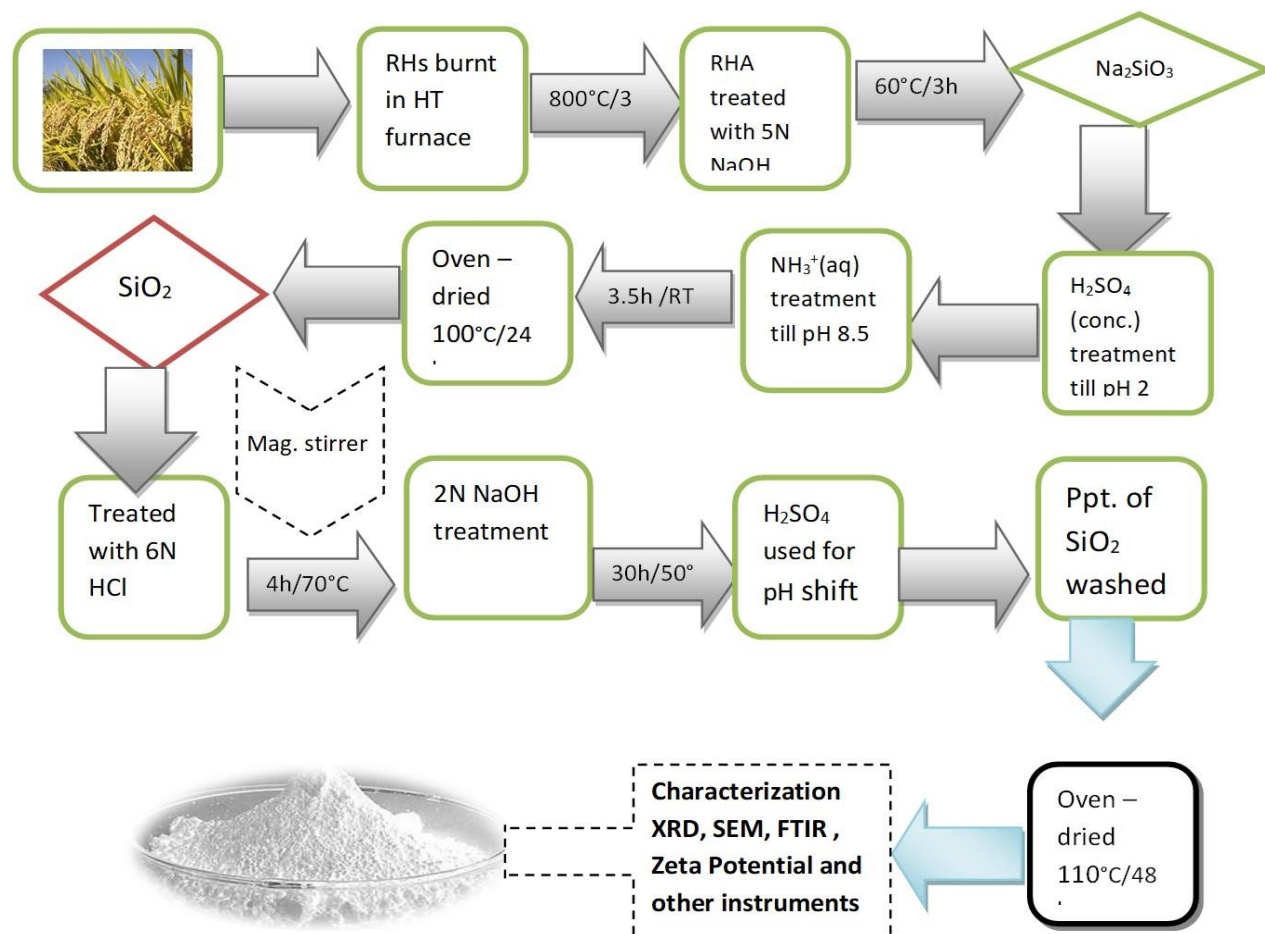

Figure 1. Flow chart for preparation of nanosilica from rice husk and agricultural waste

lignin and the removal of volatiles that were left over from the earlier stages (below 400°C) during stage 3 are responsible for the weight loss (20.14%); this process is analogous to passive pyrolysis [11, 12]. At last, the mass stabilized at a temperature of 550°C, and the remaining ash accounted for 25.57% of the measured total weight. This residue is primarily composed of silica SiO_2 and other metallic compounds, as confirmed also by a subsequent XRD measurement.

sample 2 (leached RHA) are shown in figure-3. The XRD pattern, shown in figure 3, shows the nanosilica, having an average particle size of 26 nm, using Scherrer's formula,

$t = \dfrac{0.9\lambda}{\beta \cos\theta}$, where symbol has usual meaning.

The sharp peaks show the nanomaterial prepared is in a pure very good crystalline phase and the crystal structure obtained was tetragonal [ICDD-98015-3886]. The combustion temperature of this sample was 800°C. This confirms that when
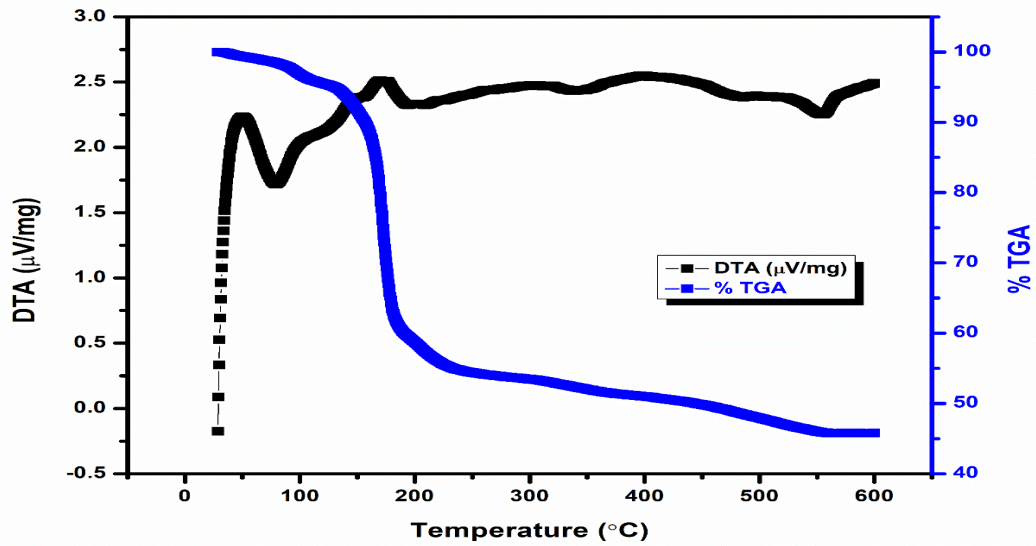
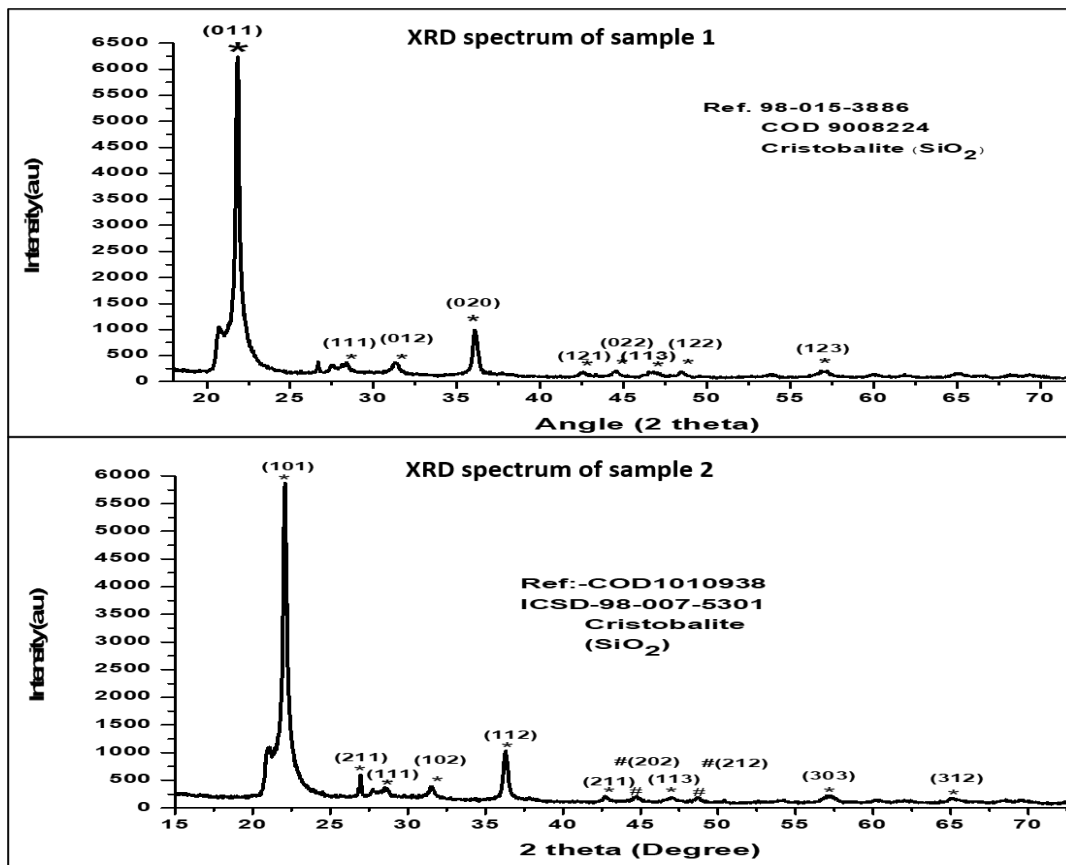**Figure 2. TGA and DTA curves for Nano-silica from rice husk**

Figure 3. XRD spectra of sample 1 and sample 2

combustion temperature exceeds 700°C then the nano-silica obtained is in crystalline form. This shows that the temperature range of 500-700°C hould be strictly maintained for amorphous

phase nanosilica production which is concluded from our earlier reported work. Amorphous phase silica has several importance [13-14]. Generally higher temperature results in crystalline structure [14]. The purity of nanosilica obtained is 60% as confirmed by XRD peak intensity curves. The XRD pattern in Figure 3 shows the crystalline form of nano-silica, having a size of 55 nm, prepared by the coprecipitation method. Here the crystal structure of the nanosilica obtained is tetragonal [15]. The broadened bases are proof of nano-phase formed. The purity of nano silica obtained is 81% as confirmed by the XRD peak intensity curve.

This sample shows more purity than the first sample-1 (raw RHA), mentioned above. Moreover, the processes involved are less time-consuming. A comparison of both the XRD pattern of rice husk prepared by the coprecipitation method and the leached method is shown in Figure 3. Both nanosilica samples are crystalline in form but vary in crystalline size. The first sample is 26 nm while the second one is 55 nm. They have different purity percentages; the second sample yielded 81% pure silica while the first sample has 60% purity. According to this research, it can be considered that the second method of synthesis is more suitable than the first where purity is concerned. While the crystalline size of the first sample is 26 nm in range, it will show enhanced properties of nano-phase and can be considered for mixing and binding substance where purity is the least consideration and the utmost concern is the nano-crystalline size and properties associated with it [16-17]. The peaks found in the XRD study demonstrate that the nanomaterials made by RHA are crystalline and that the crystals are tetragonal in form. The noticeable peak, which is seen at roughly 22 degrees, verifies the creation of nanosilica material and is precisely matched to the JCPDS file number [COD 98015-3866]. Figure 3 displays the XRD pattern, with the features hkl value also indicated in the figure, in agreement with previously published studies. This finding reveals that crystalline size and purity of percentage depend on methods of synthesis. Some research groups also reported similar results [18].

3.3. Surface morphology analysis using SEM

The SEM images of both the samples i.e., sample 1 (raw RHA) and sample 2 (leached
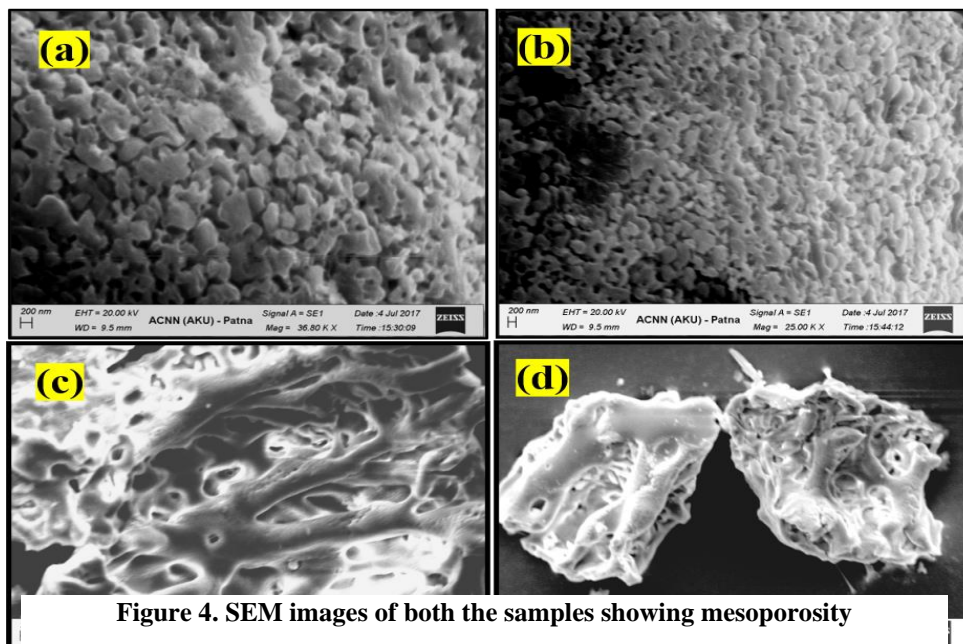

Figure 4. SEM images of both the samples showing mesoporosity

RHA) are shown in figure 4 (a,b) and (c,d) respectively and both the samples show coalescence and even distribution of the nanoparticles. The nanoparticles formed are agglomerated slightly distorted spherical and cylindrical. In addition, the SEM analyses of both samples showed porosity. The nanosilica obtained are mesoporous (2 nm - 50 nm). Nanosilica is one of the versatile classes of mesoporous materials. It has well-defined pore sizes that come with biocompatibility which can be used in a wide range of applications [19]. The surface morphology shown in the figure shows longitudinally aligned as a matrix consisting of lignin and hemicelluloses-like porous structure.

3.4. TEM Analysis: TEM have been used to further examine the silica NPs' size, shape, homogeneity, and uniformity. The nanoparticles that correspond to the sample are shown in Fig. 5 (a). The size distribution histogram was produced using the Image J program, as shown in Fig. 5 (b). In the histogram, an approximate Log-normal curve is combined. Silica nanoparticles (NPs) have a diameter of 40-50 nm and are roughly spherical. A size of 45 nm was measured for the predominant population. Agglomerates are also evident; this unavoidable phenomenon is linked to the interaction of tiny particles as a result of van der Walls forces or electrostatic attraction. The produced silica nanoparticles' modest size suggests that they can be effectively used in the right application.

3.5. FTIR measurements: The FTIR spectrum and data of the sample of both the samples, prepared by us are shown in Figure 6 and Table 1 and Table 2 respectively. FTIR results show that the peak numbers are almost at the same position, hence confirming that the same material (i.e. nanosilica) is synthesized by the two different methods. The peak numbers near 3400-3500 cm^{-1} show the presence of silanol–OH bond. The transmittance peak at 1097 cm^{-1} is due to the presence of siloxane bonds i.e. Si-O-Si bond is also present in both samples. The presence of Si-OH and other silane bond
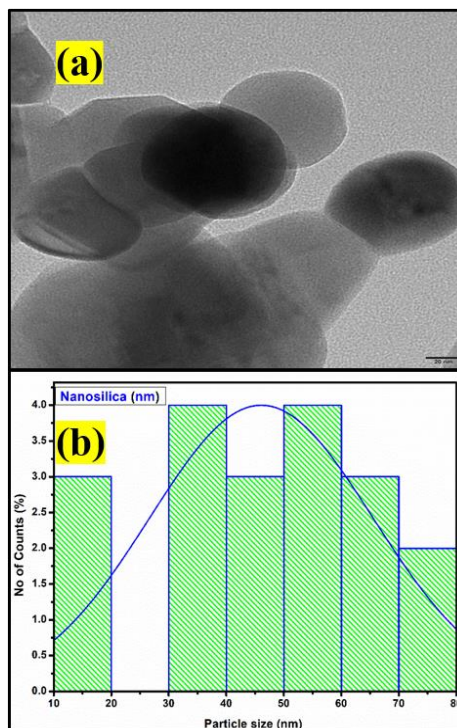

Figure 5 (a-b). TEM and histogram image of SiO$_2$ from rice husk ash

stretching vibrations are also present. The peaks between 600-800cm^{-1} are attributed to the stretching vibrations of C-H and C-Cl bonds. The FTIR graph confirms the presence of silica and is like the FTIR of nanosilca obtained in different works [20-21]. Nanosilica has a very high surface/volume ratio and contains many surface hydroxyl groups, which provide electrostatic bond energy for dye molecules on its surface. Therefore, it may be used in several applications [22].
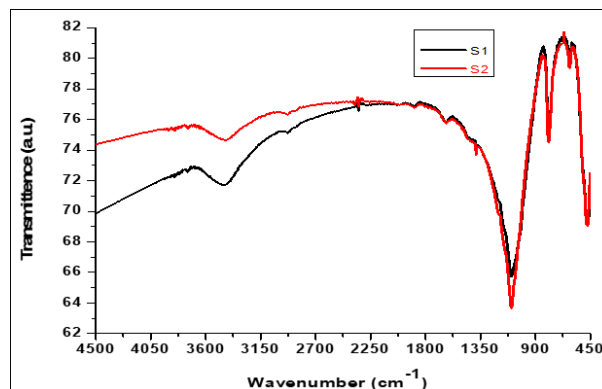

**Figure 6. The FTIR graph of sample 1 and sample 2.**

Table 1.For Sample 1 (raw RHA):

Peak Number	X (cm^{-1})- wave number	Y (%T)- transmittance
1	3436.26	74.65
2	1096.32	63.64
3	792.02	74.52
4	620.5	79.36
5	475.5	69.04

Table 2 For Sample 2 (leached RHA)

Peak Number	X (cm^{-1})- wave number	Y (%T)- transmittance
1	3460.27	71.71
2	1097.03	65.71
3	789.63	74.74
4	618.25	79.74
5	475.95	69.13

3.6. Photoluminescence Measurement: The Photo Luminescence (PL)measurements were carried out using a photoluminescence spectrometer, shown in figure 7. A 200 eV radiation source has been used as an excitation source in figure 7, the total number of peaks emitted in visible, NIR, and UV is almost the same for both Nano silica materials, synthesized by the leaching method and coprecipitate method. However, several peaks in the visible region for both samples are almost the same. This shows the PL intensity and emission were the same for samples synthesized using different methods and having different crystalline sizes. The cause of luminescence is generally due to energy band gap, defects in the crystal, types of elements present, the incident radiation wavelength used, and some other causes[23]. To the best of my knowledge to date, the PL in rice husks nanomaterial is not reported using a 200 excitation LASER source, but the PL of silicon (Si)based material was reported by some research groups [24]. The observed PL in this material can be compared with oxides of Silica. The bright luminescence may be due to the presence of silanone (Si=O) and the
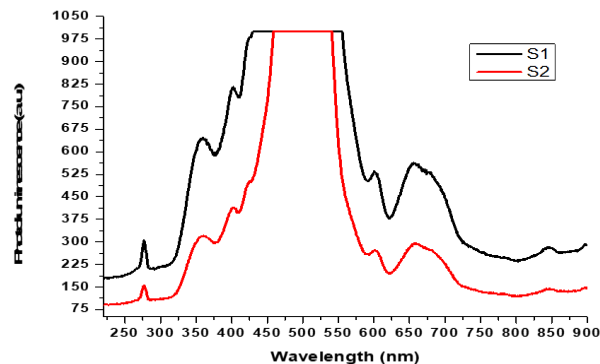
Figure 7. The Photo Luminescence Spectroscopy of sample 1 and sample 2.

dioxasilyrane, SiO$_2$ as the emitting defects are discussed in detail as prominent peaks lies in range of 455 nm and weak emissions are also seen 600 nm and 650 nm range also which is due to presence of silane bond also reported in other research group [25].

The luminescence behaviour of mesoporous silica nanoparticles shows possible applications in Bio Labelling due to luminescence behaviour. Luminescence and fluorescence imaging in Si nanoparticle imaging techniques are becoming essential in Biomedical applications and Bio nanotechnology fields. Such mesoporous structures may be potential candidates in dye removal and impurities removal from water. Zeolite and carbon nanotubes have mesoporous structures and are being used in water remediation.

3.7. Zeta Potential Measurement: Zeta potential readings were typically important for stability purposes. We discovered in this study that the silica particles have a negative charge in the pH range of 1–13. Zeta-potential measurements, which are needed to generate stable and dispersed suspensions of silica particles in water and validate the experimental conditions for the DLS measurement, are displayed in Fig-8, respectively, for various values. If the Zeta potential of every particle in suspension is high, either positive or negative, agglomeration of the particles will not occur. A common boundary between unstable and stable suspensions is +30 or -30 mV; particles with zeta
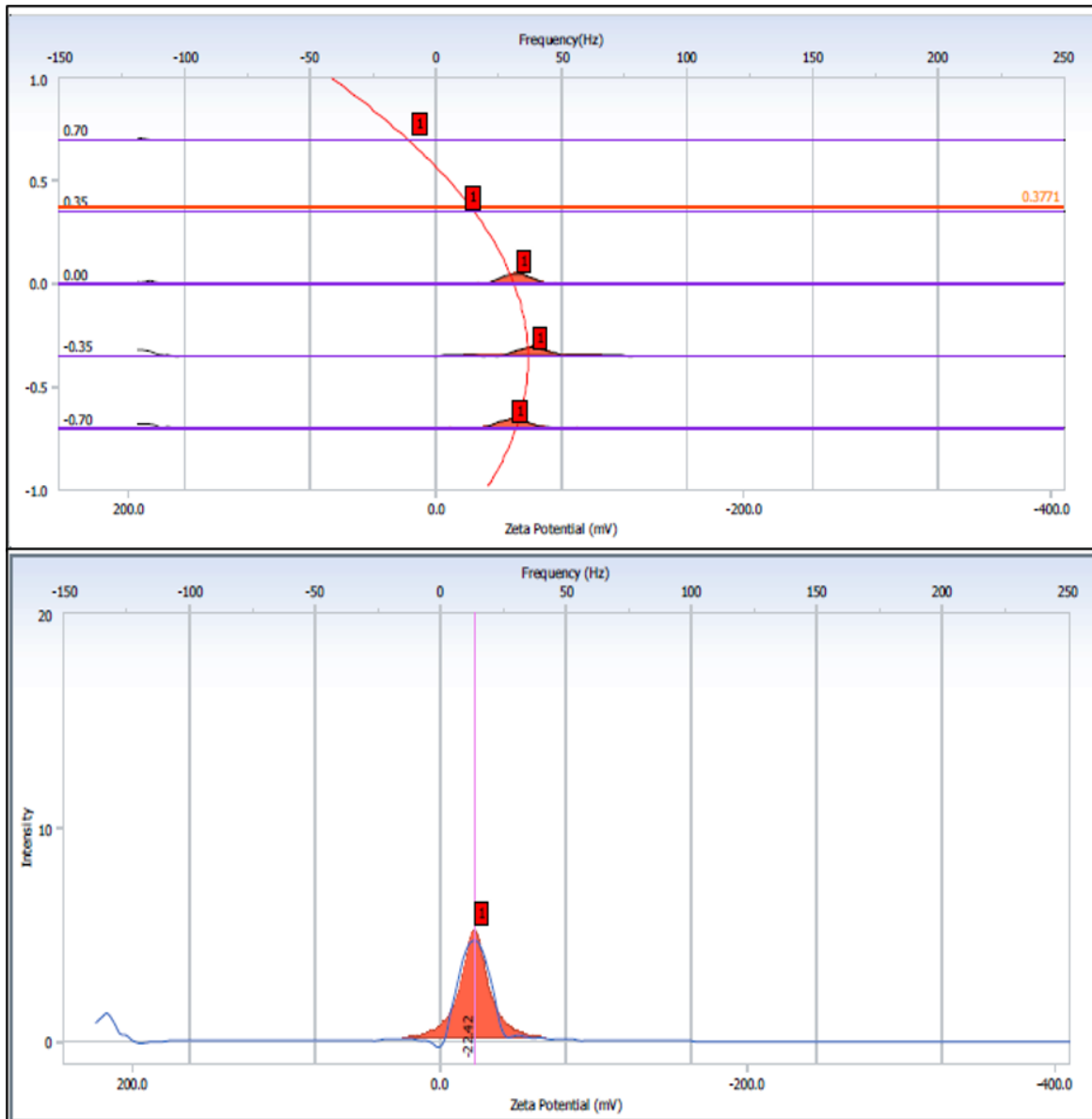
Figure 8: Zeta potential of crystalline Nano silica

potentials higher than this are frequently considered electrostatically stable. A greater zeta potential of around 25 mV is seen in all our samples, suggesting the stability of the post-synthesis suspensions. However, following the triplet experiment, the mean zeta potential displays a similar value of -22.12 mV, as indicated in Fig. 8. This Zeta potential (30.7 mV) is more than what previous writers have reported [25]. Other research groups have also reported on the use of this kind of feature for mesoporous silica drug delivery applications [26].

Conversely, the particles' durability and silica nature were shown by the negative Zeta potential, confirming their utility in drug administration.

3.8. Dynamic Light Scattering (DLS) and Particle size distributions: After the Zeta measurement, we also looked into DLS measurement to assess the particle size, which is typically more than the crystallite size as determined by XRD measurement and TEM analysis as the particle size when distributed in a liquid, as shown in figure-9.
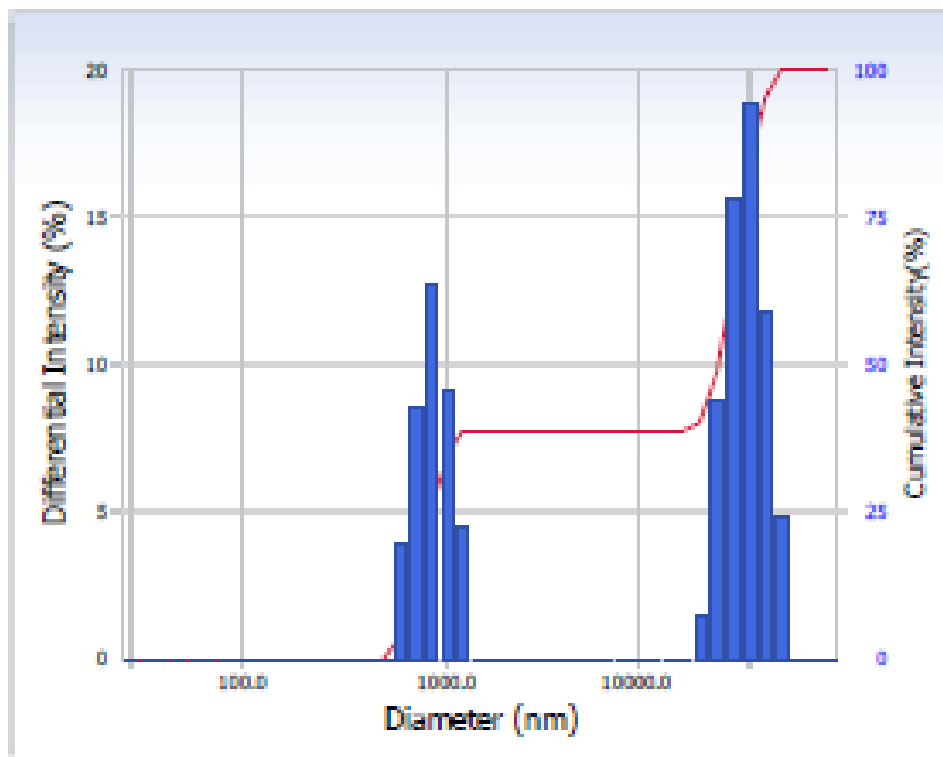
Figure 9. Hydrodynamic diameter and Concentration nanosilica

There is only one peak in width, centered at 1000 nm, and there is very little difference in the mean diameters of volume and number. Fine and coarse fractions in the dispersion are essentially non-existent, despite the size distribution in Figure 10 spanning to 1000 nm. The assertion that well dispersed somewhat spherical synthesizes silica nanoparticles is confirmed by the low value of the polydisperse index. Generally, the size measured by DLS is as hydrodynamic diameter.

4. **Conclusions:** The crystalline silica particles obtained from rice husk were found 26nm and 55nm, synthesized by both coprecipitation and leaching processes. The SEM images of both samples showed coalescence and even distribution of the nanoparticles with structural order of the pores within mesoporous, which support their use as Functional nanomaterials. The difference in purity was observed, the Leached sample showed a purity of around 80%. The infrared spectral data also supports the presence of hydrogen-bonded silanol group and the siloxane groups in the silica. Due to the strong Si-O bond, silica-based mesoporous nanoparticles are more stable to external responses such as degradation, purification of water, and mechanical stress as compared to liposomes, liposomes, and dendrimers which inhibit the need for any external stabilization in the synthesis of mesoporous silica nanoparticles. These Nano silica particles showed Photoluminescence in UV, Visible, and NIR regions. The mesoporous nanosilica obtained can be further used in drug delivery as they have low toxicity as well as high drug loading capacity, so they are used in controlled and target drug delivery systems. The Nano scale silica formation is also confirmed by TEM and DLS measurement. Zeta Potential studies reveal the stability of prepared Nano silica for a longer period.

Conflict of Interest: The authors affirm that they have no known financial or interpersonal conflicts that would have appeared to have an impact on the research presented in this study.

References:
[1] Z.L. Wang, R.P. Gao, J.L. Gole, and J.D. Stout, Silica nanotubes and nanofiber arrays, J. Adv. Mater. 12, 2000, 1938–1940.
[2] Z. Li, J. Zhang, J. Du, B. Han, and J. Wang, Preparation of silica microrods with nano-sized pores in ionic liquid microemulsions, Colloids Surf. A: Physicochem. Eng. Aspects 286, 2006, 117–120.
[3] R. Manivannan and S. Ramanathan, The effect of hydrogen peroxide on polishing removal rate in CMP with various abrasives, Appl. Surf. Sci. 255, 2009, 3764–3768.
[4] J. Zhang, L.-M. Postovit, and D. Wang, In situ loading of basic fibroblast growth factor within porous silica nanoparticles for a prolonged release, Nanoscale Res. Lett. 4, 2009, 1297–1302.
[5] W. Zhang and M. Zhao, Fluidisation behaviour of silica nanoparticles under horizontal vibration, J. Exp. Nanosci. 5, 2010, 69–82.
[6] F. Torney, B.G. Trewyn, V.S.Y. Lin, and K. Wang, Mesoporous silica nanoparticles deliver DNA and chemicals into plants, Nat. Nanotechnol. 2, 2007, 295–300.
[7] M.L. Liu, D.A. Yang, and Y.F. Qu, Effect of different chemical additives and heat-treatment on ambient pressure dried silica aerogels, J. Exp. Nanosci. 5, 2010, 83–91.
[8] M. Tomozawa, D.L. Kim, and V. Lou, Preparation of high purity, low water content fused silica glass, J. Non-Cryst. Solids 296, 2001, 102–106.
[9] P.A. Tanner, B. Yan, and H. Zhang, Preparation and luminescence properties of sol–gel hybrid materials incorporated with europium complexes, J. Mater. Sci. 35, 2000, 4325–4328.
[10] G. Wu, J. Wang, J. Shen, T. Yang, Q. Zhang, B. Zhou, Z. Deng, F. Bin, D. Zhou, and F. Zhang, Properties of sol–gel derived scratch-resistant nano-porous silica films by a mixed atmosphere treatment, J. Non-Cryst.Solids 275, 2000, 169–174
[11] Pijarn, N.; Jaroenworaluck, A.; Sunsaneeyametha, W.; Stevens, R., "Synthesis and characterization of nanosized-silica gels formed under controlled conditions," Powder Technol., 203, 2010, 462-467.
[12] Liou, T. H., "Evolution of chemistry and morphology during the carbonization and combustion of rice husk," Carbon N. Y., 42, 2004, 78-83
[13] P. Mishra, A. Chakraverty, and H.D. Banerjee, Production and purification of silicon by calcium reduction of ricehusk white ash, J. Mater. Sci. 20, 1985, 4387–4391.
[14] A. Chakraverty, P. Mishra, and H.D. Banerjee, Investigation of combustion of raw and acid-leached rice husk for production of pure amorphous white silica, J. Mater. Sci. 23 1988, 21–24.
[15] J. James and M. Subba Rao, Silica from rice husk through thermal decomposition, Thermochim. Acta 97, 1986, 329–336.
[16] K. Kamiya, A. Oka, and H. Nasu, Comparative study of structure of silica gels from different sources, J. Sol–Gel Sci. Technol. 19, 2000, 495–499.
[17] K.G. Mansaray and A.E. Ghaly, Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis, Biomass Bioenergy 17, 1999, 19–31.
[18] N. Yalcin and V. Sevinc, Studies on silica obtained from rice husk, Ceram. Int. 27 2001, 219–224.
[19] T.H. Liou, Preparation and characterization of nano-structured silica from rice husk, Mater. Sci. Eng.: A 364, 2004, 313–323.
[20] R.R. Zaky, M.M. Hessien, and A.A. El-Midany, Preparation of silica nanoparticles from semi-burned rice straw ash, Powder Technol. 185 2008, 31–35.
[21] C. Real, M.D. Alcala, and J.M. Criado, Preparation of silica from rice husks, J. Am. Ceram. Soc. 79, 1996, 2012–2016.

[22] R. Conradt, P. Pimkhaokham, and U. Leela-Adison, Nano-structured silica from rice husk, J. Non-Cryst. Solids 145, 1992, 75–79

[23] G.F. Luo, W.H. Chen, Y. Liu, Q. Lei, R.X. Zhuo, X.Z. Zhang, Multifunctional enveloped mesoporous silica nanoparticles for subcellular co-delivery of drug and therapeutic peptide, Sci. Rep. 4, 2014 6064-6049.

[24] Naiara I. Vazquez, Zoilo Gonzalez, Beg˜ona Ferrari, Yolanda Castro Synthesis of mesoporous silica nanoparticles by sol–gel as nanocontainer for future drug delivery applications, Bol. Soc. Espanola Ceram. Vidr. 5, 2017, 139–145

[25] M.S. Dhlaminia, J.J. Terblansa, R.E. Kroona, O.M. Ntwaeaborwaa, J.M. Ngaruiyaa, J.R. Bothab and H.C. Swarta, Photoluminescence properties of SiO2 surface-passivated PbS
Nanoparticles, South African Journal of Science 104, 2008, 397-400.

[25] Samira Jafari , Hossein Derakhshankhah , Loghman Alaei , Ali Fattahi , Behrang Shiri Varnamkhasti , Ali Akbar Saboury, Mesoporous silica nanoparticles for therapeutic/ diagnostic applications, Biomedicine & Pharmacotherapy, 109, 2019, 1100-1111

[26] Naiara I. Vazquez, Zoilo Gonzalez, Beg˜ona Ferrari, Yolanda Castro Synthesis of mesoporous silica nanoparticles by sol–gel as nanocontainer for future drug delivery applications, Bol. Soc. Espanola Ceram. Vidr. 5, (2017), 139–145.