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Rice husks as a sustainable source of high quality nanostructured silica for high performance Li-ion battery requital by sol-gel method – a review

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ABSTRACT

The electronics industry is heavily reliant on the use of silicon in devices ranging from solar panels to circuitry. This is of growing concern due to the environmental impact of sourcing and refining the material. Thus, a green source of silicon is of vital importance to meet the growing demand for silicon in the industry. Rice husk represents an abundant source of nano silica. Currently the husk is considered a waste product that is separated from the grain during the milling process. Several methods have been trailed to extract the nano silica from rice husk. This paper reviews these current methods and presents suggestions of innovative research directions for processing techniques. This work reveals that the structural nature of superfine silica from rice husk ash is independent of the purification method, but dependent on the incineration temperature used. The paper concludes by advocating the physic-chemical process for producing high purity reactive nanosilica from rice husk. This method has the advantage of having high volume production versatility and being environmentally friendly. However, control of the morphology, shape, size, crystalline structure and chemical composition of rice husk nanostructures remains a challenge in the development of 3D nanopores arrays controllable by synthesis methods. We hope this article can provide the reader with snapshots of the recent development and future challenges.

Keywords: Rice husk ash; NSi; XRD; FTIR; PL spectra.

Introduction

Worldwide concerns over energy related climate change coupled with the spiraling cost of fossil fuels in recent years has increased interests in renewable energy alternatives. Although solar photovoltaic power generation is a proven technology, especially in the space industry, development of this technology to meet terrestrial energy demands has been limited. During the last two decades, 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 green-house gases [**1**]. Fossil fuel shortage and energy environmental problems have created the urgency for the exploration of clean renewable energies [**2**]. As a result, many countries have put forward plans to reduce carbon dioxide emissions and energy consumption. Biomass is one of the most promising energy carrying agents and plays an important role in environmentally friendly energy utilization [**3**]. Rice husk is a form of agricultural biomass that provides highly efficient thermal energy and an abundant lignocelluloses source for preparing bio-oils [**4**]. The annual global product of rice husk is approximately 1 million tons [**5**] (**Fig. 1**). The major constituents of rice husk are hydrated silicon and organic materials consisting of cellulose of 55-60 wt % including cellulose and hemicelluloses and 22 wt % of lignin. The white ash as obtained from combustion of this raw material at moderate temperature contains 87-97 % silica in amorphous form and some amount of metallic impurities [**6**]. This product is not suitable for human consumption. The disposal of the ashes and partially bored husk creates environmental hazards [**7-9**]. One interesting application of rice husk is the production of silica nanoparticles at low cost and high efficiency [**10**]. Silica is an important ingredient of high surface area catalyst, absorption media, glass and cement manufacturing and dehydration system which is complicated and tedious [**11-13**]. The rice husk, coming out of rice mills represents a cheap hydro product with great opportunity for the production of silica at nominal expenses. At present nano-silica materials are prepared using several methods such as vapor phase reaction (VPR), sol-gel and thermal decomposition technique (TDT). Recently, nano-structured silica powders with high specific area were obtained from non isothermal decomposition of rice husk under air atmosphere [**14**]. The effect of temperature on phase transitions of nanocrystallize silica obtained from rice husk are previously less reported [**15**]. Additionally, the production of silica nano particles by californian–Red worms through a bio-digestions process was reported by Estevez *et al.* [**16**]. In addition to this, silica has been used for gene delivery to obtain more efficient DNA delivery vectors for both basic research and clinical trials [**17**]. Kalapathy *et al.* [**18**] investigated aerogel formation using rice husks as raw material dissolved with NaOH and the incorporation of acid washing enhances the purity of the sample. Zhang *et al.* [**19**] used rice husk as a precursor, obtaining superfine silica with a diameter of 30-100 nm. Recent studies have produced silica nanoparticles by rice husk biotransformation using fusarium oxysporum fungus [**20**]. Witoon *et al.* [**21**] used rice husk ash as a raw materials and chitosan as a template to prepare bimodal porous silica. Real *et al.* [**22**] found that a homogeneous size distribution of nanometric silica particles could be obtained by dropping rice husk at 873-1073 K in a pure oxygen atmosphere. Della *et al.* [**23**] observed that active silica with a high specific area could be produced from rice husk ash after heat treating at 973 K in air. Karmath *et al.* [**24**] reported that the rice husk could be dissolved in NaOH solution to obtain silica gel. Farook Adam *et al.* [**25**] fabricated silica-tin nanotubes from rice husk ash using a sol-gel method using cetyltriethylammonium bromide (CTAB) as a surfactant at room temperature (RT). It is interesting to develop an economically viable method to extract nanosilica from silicon containing biomass material. The previous studies were focused on the process of manufacturing silica from rice husk. Spherical and needle like cobalt nanoparticles impregnated on rice husk silica was also synthesized by Farook Adam *et al.* [**26**]. The saturation magnetization and coercive force of rice husk nanoparticles were found to be 0.245emu/g and 304.09 respectively. The reinforcing effect of hybrid filler including rice husk, beech bark and nano SiO_2 in polypropylene were investigated by Amir Nourbakhsh *et al.* [**27**]. The preparation of semiconductor grade carbon using pyrolysis technique from rice husk has been reported by Subama Maiti *et al.* [**28**]. In either forms, rice husk has some applications. Among the uses reported are pozzolan in cement industry [**29-35**], aerogels [**36, 37**], SiC [**38, 39**], porous carbon [**40**], zeolites [**41**] and cordierite [**42**]. In earlier work, we reported an indirect use of rice husk in making insulating refractories [**43, 44**]. These uses are related to the processing route or method used, which often affect the product characteristics. For example, it has been shown that different methods of preparation of rice husk silica produce different morphology, structure and

Fig. 1. Schematic diagram of paddy grown on a farm land and rice husks which is a natural reservoir of silica nanoparticles.

reactivity [**45-47**]. The most reviews on this subject were in 2003 and 2001, and thus do not incorporate the dramatic technological developments that have occurred since this time. This paper is therefore an attempt to review the research depth and directions of the processing methods as well as the characteristics and utilization of rice husk silica in these intervening years. The paper presents a critical review of the literature by assessing the current production facilities and processes in the field as well as the influence each process has on the product characteristics. It ends by making the case for a process currently being developed, which is called the hydrothermal process. It is our hypothesis that this process would be inexpensive and versatile with regard to the effects it would have on the quality of rice husk silica produced by varying the process parameters.

Processing of rice husk for silica various method

Different processes have been used by different researchers to obtain silica from rice husk (**Fig. 2**). The following discussion reviews these processes, highlighting their advantages and disadvantages.

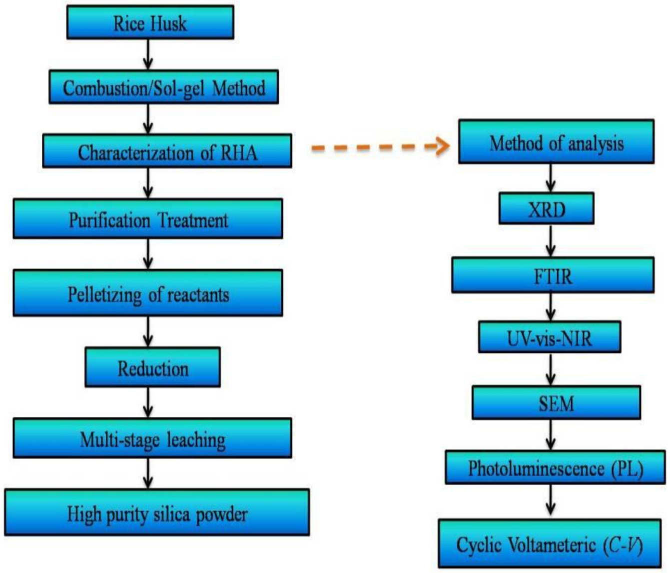

Fig. 2. Schematic diagram of experimental work.

Composition of rice husk ash

There are many reports [**48-50**] on the varying composition of rice husk ash which is largely dependent on a number of factors. These include but are not limited to, agricultural practices such as the use of fertilizers during rice cultivation, type of fertilizers employed and climatic or geographical factors. Thus, depending on the geographical location, different authors have published different values for the composition of rice husk. The methods used to evaluate the composition quoted are also indicated. It is clear that though the composition of rice husk may be dependent on several factors, the percentage of silica (SiO_2) in the ash ranges between 87-92%. A trace amount of Titania (TiO_2) was also reported [**51**]. Due to this compositional variation, the suitability of rice husk silica for any given application will therefore be largely dependent on the purity level needed and if it is not met from the beginning for a given application, then a purification process will be carried out to reduce or eliminate unwanted impurities.

Physico-chemical method

The physic-chemical method is a two steps process that involves alkali solubilization and acidic precipitation was adopted. For alkali solubilization it is proposed that silica present in RH dissolves in sodium hydroxide to produce sodium silicate solution. Here in this equation x is the ratio of SiO_2 to Na_2O in the sodium silicate solution. For acidic precipitation the sodium silicate reacts with nitric acid to produce silica gel. The as-obtained solution of sodium silicate was titrated with 3 M/lit of HNO_3 with drop wise at a rate of 9 M/minute with constant stirring, so that the pH curve for this titration is sigmoid with a sharp change occurring at pH 4.3. The midpoint of the curve was pH 4 which is the end point of the reaction. Then the resulting gel was kept for 7 days. The as-obtained gel was centrifuged at 500 rpm, filtered and washed with distilled water. The final washing was done with acetone. After washing it was dried at 370 °C for 24 hrs. The dried powder was then grounded into a fine powder which was yellow in color. After that the powder was kept in an autoclave at a temperature of 170 °C for 18 hrs. In subsequently the powder was cooled to room temperature and finally washed with ethanol. The resultant powder was again heated at 130 °C for 15 hrs. PEG-6000 was added into sodium silicate solution (PEG-6000, 5 ml) and stirred to dissolve completely. The as-obtained powder was designated as Nanosilica (*NSi*) (**Fig. 3**). (Dr. K. Kaviyarasu & Prof. M. Maaza unpublished work).

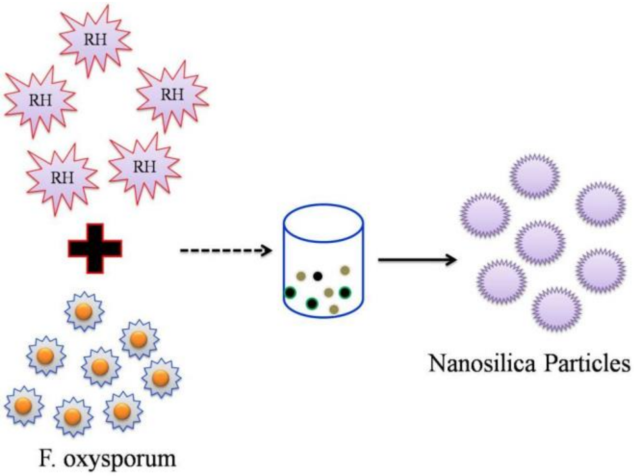

Fig. 3. Schematic diagram of reaction processing work.

Hydrothermal method

Hydrothermal synthesis has been defined as a process that utilizes single- or heterogeneous phase reactions in aqueous media at elevated temperature ($T>25$ °C) and pressure ($P>100$ kPa) to crystallize ceramic materials directly from solution. As stated in the introduction, rice husk contains organic compounds and oxides of metals. Under high temperature, high pressure and acidic or basic medium with strong oxidizing activity, the organic compounds are decomposed and the trace metals turned into soluble ions;

then, silica obtained. This processing method can achieve the purification of silica from the husk with only the use of water. However, achieving complete dissolution of the organic matter in the rice husk is a task that is near impossible. So, practically this process still requires an incineration step, though the soaking time may be less compared to incinerating the untreated or pre-treated rice husk. The method does not affect the amorphicity of the silica in rice husk. Some acids with strong oxidizing activity such as H_2SO_4 and HNO_3 are used and sometimes H_2O_2 is also used as the oxidative medium. This method had been used by Mochidzuki *et al.* [**52**].

Thermal evaporation method

The rice husks used were obtained from rice mills. They were further washed with tap water to remove soils and dirt, and dried in the sun. The dried husks were washed with distilled water and dried again in an oven at 60 °C. The dried husks were chemically treated with 37 % HCL (E-Merck company). The HCL was diluted with distilled water to achieve a HCL solution with a 1% molar concentration.

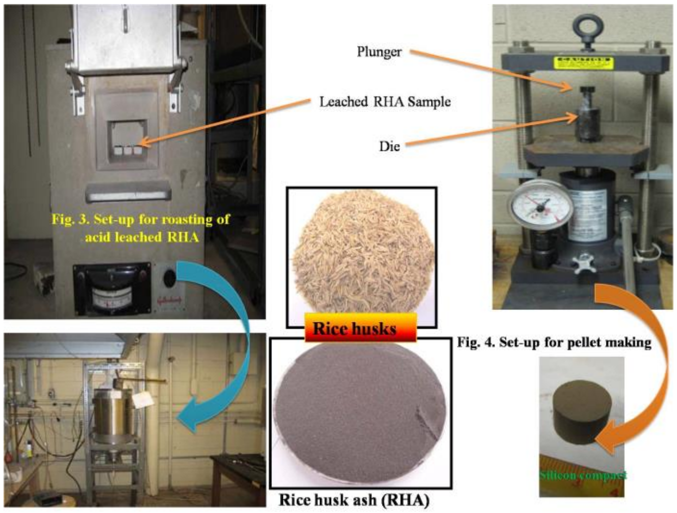

Fig. 4. Schematic diagram of mechanism work.

The rice husks mixed with the HCL solution in a glass beaker that was placed on hot plate at 90 °C for 1 hour (**Fig. 4**). The solution was filtered and the rice husks were washed with distilled water several times until they were acid-free. The acid-leached rice husks were dried in an oven at 60 °C. They were fired at 600 °C in air for 3 hrs. A coconut shell was cleaned with tap water and distilled water several times and dried in oven at 60 °C. The cleaned coconut shell was burned at 400 °C in normal atmosphere to charcoal. The coconut shell charcoal was ground to fine powder and put in a glass beaker. The 1 molar HCL was poured in the beaker and the charcoal was soaked for 3 hrs. The solution was filtered and the charcoal powder was washed with distilled water several times until acid-free. The rice husk ash consisted >99% amorphous silica. The coconut shell charcoal comprised of >70% of carbon. The source materials were mixed so that a ratio of cleaned rice husk ash and coconut shell charcoal was obtained. They were ground together to form powder mixtures. The powder mixtures were put in an alumina boat and then Si substrates were placed on the powder mixtures. The alumina boat and source materials were placed in the middle of quartz tube furnace. They were heated at 1250 °C in one atmosphere of nitrogen with a flow rate of 2L/min for 1 hour. Afterward, the furnace was cooled down to room temperature naturally.

Bioactivity of silica-based ceramics

Silica plays an integral role in the bioactivity and osteogenic potential of Bioglass, as shown by Yalcin *et al.* [**53**]. They suggested that the high density of surface silanol groups (Si-OH) that exist on amorphous silica is the basis for enhanced hydroxyapatite (HAp) and bone formation in bioglass and related glass ceramic systems. The silanol groups are proposed to be very effective at inducing HAp formation [**54**]. Hypothesis on physiological silicon research was developed by Bose *et al.* [**55**] and Segal *et al.* [**56**]. Silicic acid is essential for the healthy growth of bone and connective tissue. They conclude that the interaction of silicic acid with many metals in vivo produces positive health effects. Silverstein *et al.* [**57**] suggested on the bioactivity of amorphous silica. Silica is present in aquatic organisms, the protruding spicules of certain sponges, and the teeth of certain mollusks. These biosilicates are made up of particulate or solid-gel silica with species-specific sizes, shapes, and aggregate arrangements. Singh *et al.* [**58**] pointed out that, silica based materials provide an additional parameter in the form of biologically active, soluble SiO_2, which is known to affect such as osteoblast activity. Sharma *et al.* [**59**] also suggested that amorphous silica owing to its bioactivity is used in medical devices. Sharma *et al.* [**60**] reported that silica-gel samples with high volume percentage porosity and pore size >2 nm are suitable for inducing *in vitro* hydroxycarbonate apatite (HCA) formation in simulated body solutions. Krishnarao *et al.* [**61**] pointed out that amorphous silica is biocompatible and degradable in living tissue, as well as in corresponding simulated physiological conditions. Bharadwaj *et al.* [**62**] studied the toxicity of silica over silica based hybrid material. They proved that the sol-gel silica coating of material is biocompatible and non-toxic, and the response of cells such as osteoblasts to silica gels was quite good as identified by Liou *et al.* [**63**]. Several authors suggested that silica nanoparticles are biocompatible and degrade over time in the body [**64-66**]. The biocompatibility of silica precursor was monitored by Shim *et al.* [**67**]. It was also shown by Liu *et al.* [**68**] that tetraalkoxysilanes can be successfully exchanged for tetrakis (2-hydroxyethyl) orthosilicate (THEOS). Several researchers like Wu *et al.* [69], Gu *et al.* [**70**] and Kovalenko *et al.* [**71**] suggested that silica xerogel prepared from alkoxysilane can be coated on titanium at room temperature, especially for cardiovascular therapeutic applications. The silica xerogel system is an attractive material to apply to metallic substrates, because sol-gel derived silica xerogels are known to have excellent bioactivity and exhibit chemical bonding to the surrounding tissues, particularly bone. Tian *et al.* [**72**] reported that, porous silica gels obtained from TEOS and polyacrylic acids (PAA) are bioactive *in vitro*. Hochbaum *et al.* [**73**] studied the cell viability in a wet silica gel, made from TEOS and found that the cells can stay alive within the gel.

Boukai *et al.* [**74**] also studied the bone bonding ability of silica gel with respect to the synthesis temperature of the gel. That found that the lower temperature treatment at 400 °C and 600 °C allowed the silica gels to be degraded easily, while gels treated at 800 °C and 1000 °C were more stable. Many researchers were suggested that sol-gel derived silicas are potential biomaterials and they have been studied both for tissue regeneration and drug delivery applications. They are used either in a pure SiO_2 gel form or in the form of composites [**75-77**]. Wu *et al.* [**78**] observed that, no changes in liver, kidney, uterus or lymph nodes related to silica xerogel, even though the applied amount of silica xerogel was high. Recently, some reviews were reported on sol-gel silica and hybrid biomaterials and the processes of biosilicification [**79-81**]. Novel synthetic approaches, allowing the immobilization of enzymes, living cells, antibodies, immune molecules, polysaccharides, phospholipids, nucleic acids, proteins and other biomolecules in the sol-gel matrices, have been proposed. Lee *et al.* [**82**] studied prospects of silica based hybrid materials for glucose sensor. This hybrid material was found to be non-toxic and also slows down the growth of fibroblasts on its surface, which is important since a thick capsule could inhibit the diffusion of glucose to an implanted glucose sensor [**83-85**]. Many researchers including Morales *et al.* [**86**] and Geohegan *et al.* [**87**] studied the dissolution features of glass and glass-ceramics in SBF medium. Silica is a biodegradable material as stated by Wang *et al.* [**88**] and proved by other researchers. Nagamori *et al.* [**89**] studied the dissolution characteristics of bioactive titanium-particle-containing dicalcium silicate coating in tris-hydroxy methyl amino methane (TRIS) buffered solution. Dissolution study of porous poly (DL-lactide-co-glycolide) (PLGA)/bioactive glass composite was carried out in TRIS medium by Bao *et al.* [**90**]. Similar dissolution features of zinc-containing bioactive glasses in TRIS medium was also studied by Gu *et al.* [**91**].

Silica aerogel

Aerogels, which are highly porous, low-density materials consisting of nano-sized pores, are of interests for applications as varied as thermal insulation, catalysis, drug delivery, etc [**92**]. The synthesis of silica aerogel can be divided into three general steps, which are (a) preparation of gel, (b) ageing of gel, and (c) drying of gel. In the first step, colloidal system of liquid character is changed into colloidal system of solid character whereby the dispersed substance forms a continuous, coherent framework that is interpenetrated by liquid. The gel prepared is aged in its mother solution to strengthen the gel, so that shrinkage during the drying step will be minimum. In the last step, the gel should be freed of the pore liquid. To prevent the collapse of the gel structure, special precautions are taken during the drying. Liu in 2011[**93**] first attempted the preparation of silica aerogel by removing the liquid from a gel by a gas (air). The liquid held inside the gel has greater pressure than its vapour. To transform this liquid into a supercritical fluid (gas), a certain temperature is required which is known as the critical temperature. Above that critical temperature the air can replace the supercritical fluid to produce get a non-collapsed gel structure [**94**]. During drying under atmospheric conditions, the nanostructured porous layers are exposed to capillary force and large surface tension, which destroys the microstructure and cause the shrinkage of the gel [**95**]. Supercritical drying (SCD) method is usually used to solve this problem. In this process, the liquid in a substance is transformed into gas in the absence of surface tension and capillary stress. Thus, no damage occurs to the material's delicate nanostructured pore network. However, the SCD is a relatively expensive process due to its high-pressure operating condition. For this reason, there is a great interest in subcritical or ambient pressure drying. Ambient-pressure methods for silica aerogel include both surface modification and network strengthening of sol-gel derived silica wet gel. To prepare the silica gel, silicon alkoxides like, tetramethoxysilane (TMOS) tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and polyethoxydisiloxane (PEDS) are mainly used [**96-99**]. In Ambient-pressure method, the water-alcohol mixture in the pores of the gel is first exchanged for a water-free solvent. Then, reaction with salivating agent takes place so that Si-OH groups are salivated. Salivation is carried out directly in the water phase of the hydrogel, which results in a solvent exchange as well as a phase separation of the gel water and the solvent. The replacement of -H from the Si-OH groups by the hydrolytically stable Si-R groups through the oxygen bond prevents the adsorption of water and hence results in the hydrophobic aerogels [**100**]. Washing in H_2O/ethanol (EtOH) increases the liquid permeability of the solid part of the gel by a dissolution reprecipitation process for silica. Aging in a siloxane solution increases the stiffness and strength of the alcogel by adding new monomers to the silica network as stated by Ikram *et al.* [**101**]. Bathey *et al.* [**102**] removed the pore water through exchanging for OH and *n*-heptane. All the silicon alkoxides materials are not only expensive but also hazardous and can cause blindness (with TMOS). To avoid the cost of raw materials, Bullis et al [**103**] used water glass as a cheaper silica source. Water glass (or sodium silicate) solution was used for low-cost aerogel production by Goetzberger [**104**] using super critical drying method. Water glass based aerogels were also prepared by Goetzberger [**105**], Pizzini [**106**], Dietl [**107**] and others using SCD method. Gribov *et al.* [**108**] investigated properties of aerogels synthesized by different precursors and reported that water glass, produced aerogel with the highest degree of monolithicity because these gels had the highest stiffness and the largest pore size. In the case of water glass based aerogel, the sol-gel preparation is quite different. The sol in this case is silicic acid (H_2SiO_3) which is produced by exchanging Na^+ ions of water glass with H^+. To remove sodium ions in the water glass, the dilute sodium silicate is passed through ion-exchange column filled with strong acidic cation resin such as, sulphonated polystyrene. Adopting this ion exchanging technique, Istratov *et al.* [**109**] and Fang *et al.* [**110**] have prepared silica aerogel. But, Bose *et al.* [**111**] had removed the sodium portion from the silica aerogel beads by washing with distilled water for 12 hrs. The silica aerogel prepared in this study used as ambient pressure drying method with sodium silicate as the silica precursor. Singh *et al.* [**112**] prepared silica aerogel from RHA by sol-gel process, followed by supercritical drying. A new process for preparing silica aerogel was proposed. RHA, which is not only cheap but also rich in silica, was used as the silicon source. Hunt [**113**] prepared the aerogel through sol-gel process using RHA; a small quantity of TEOS was used as the modifier, and added into the hydro-sol. Then the aerogel was prepared by drying the gel at atmospheric pressure. Several authors have suggested that silica aerogel is a promising biocompatible scaffold for the immobilization of biological material for a variety of applications and as matrices in the design of biosensors [**114-116**]. Bhardwaj *et al*. [**117**] studied the preparation and bioactivity of wollastonite/aerogels composites obtained from a TEOS-MTES matrix through the sol gel process. Bioactivity of this aerogel was studied by immersing it in SBF for 25 days. A spherical apatite layer covered the entire surface of the aerogel. Madsen *et al* [**118**] prepared protein encapsulated silica aerogel to form bioaerogel via the sol-gel polymerization of TEOS with an ionic liquid as the solvent and pore-forming agent and the solvent extraction process (**Fig. 5**). The final gel was dried through Freeze-drying process.

Properties of nanosilica rice husk

In this section the properties of nanosilica rice husk are examined, in particular the production process employed affects factors such as the electrical and mechanical properties.

Chemical analysis

Chemical analysis of raw husk, Brown Ash (BA), White Ash (WA) and Silica Gel (SG) was carried out using XRD. **Table 1**, shows the chemical composition (oxide basis) of three silica precursors. BA contains approximately 96% SiO_2 and the remaining consists of 4% oxides of potassium, calcium, iron, zinc, and manganese. Except SiO_2, all other oxides may be considered as impurities. The brown color of BA is attributed to the presence of these impurities. WA contains nearly pure SiO_2 (99.87%). It was prepared from husks that were thoroughly acid leached. The acid leaching was effective in removing most of the impurities stated above for BA. The silica content of SG was found to be about 99.78%. The SG was prepared through alkali extraction of amorphous silica from BA, and then by acid neutralization of silicate solution to form gels. The impurities were low in SG compared to BA, because they were partially removed during the processing of the gel.

Table 1. Chemical analysis of Silica precursors (mass %).

Oxides	Raw Husk	Brown Ash	Silica Gel	White Ash
Organic matter	75.6			
$Si0_2$	17.26	96.01	99.79	99.87
K_2O	0.28	0.86	-	-
CaO	1.11	2.22	0.13	-
Fe_2O_3	2.86	0.57	0.03	0.13
Al_2O_3	1.37			
ZnO	0.67	0.06	0.05	-
Na_2O	0.84			
Mn_2O_3	0.11	0.28	-	-

Experimental

Materials and methods

Rice husk ash (RHA) was obtained from a local rice milling plant in kannamangalam & Salamanatham villages, Vellore District, Tamil Nadu, India. Sodium hydroxide (E-Merck 99.99%), Nitric acid (E-Merck 99.99%), (E-Merck 99.99%), cetyltriethylammonium bromide (CTAB) and Acetone (E-Merck 99.99%) of analytical grade were used without further purification. Stoichiometric quantities of RHA, sodium hydroxide, and nitric acid were used to process the RHA.

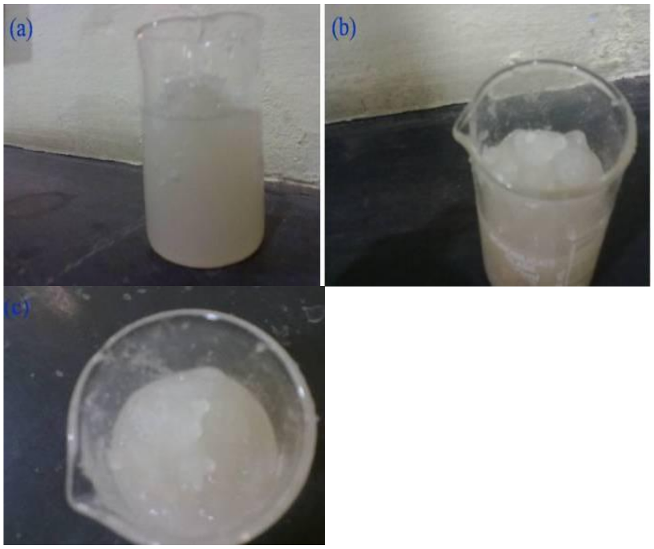

Fig. 5. Nanosilica rice husk sol-gel images.

The two step process involving alkali solubilization and acidic precipitation was adopted. For alkali solubilization it is proposed that silica present in RHA dissolves in sodium hydroxide to produce sodium silicate solution.

$$xSiO_2+2NaOH \longrightarrow Na_2OxSiO_2+H_2O \tag{1}$$

Here in this equation x is the ratio of SiO_2 to Na_2O in the sodium silicate solution. For acidic precipitation the sodium silicate reacts with nitric acid to produce silica gel.

$$Na_2OxSiO_2+HNO_3 \longrightarrow SiO_2+Na_2NO_3+H_2O \tag{2}$$

The as-obtained solution of sodium silicate was titrated with 3 M/lit of HNO_3 at a rate of 7 M/minute with constant stirring, so that the pH curve for this titration is sigmoid with a sharp change occurring at pH ~ 4. The midpoint of the curve was pH ~ 3 which is the end point of the reaction. Then the resulting gel was kept for 5 days to age. The as-obtained gel was centrifuged at 400 rpm, filtered and washed with distilled water. The final product washing was done with acetone. After washing it was dried at 310 °C for 24 hrs. Again the dried powder was grounded into a fine powder which was yellow in color. The powder was then transferred to an autoclave and held at a temperature of 150 °C for 18 hrs. Subsequently the powder was cooled to room temperature and finally washed with ethanol three times. The resultant powder was again heated at 110 °C for 12 hrs. 5 ml of cetyltriethylammonium bromide (CTAB) was added into sodium silicate solution and stirred to dissolve completely. The as-obtained powder was designated as nanosilica (**Fig. 6 and 7**).

Characterization studies

The as obtained NSi was placed on the sample holder and leveled to obtain total and uniform X-ray exposure. The samples were analyzed by X-ray diffraction (XRD). The instrument used was Richseifert X-ray diffractometer, Cukα radiation (λ=1.5418 Å) in the range of 10° - 70° in steps of 0.04′ at a scan speed 2°/min [**119, 120**]. The above study was carried out to confirm the crystallinity of the sample. UV-vis-NIR spectra NSi nanocrystals were recorded by a UV-vis-NIR, spectrophotometer (JASCO V-550, Japan).

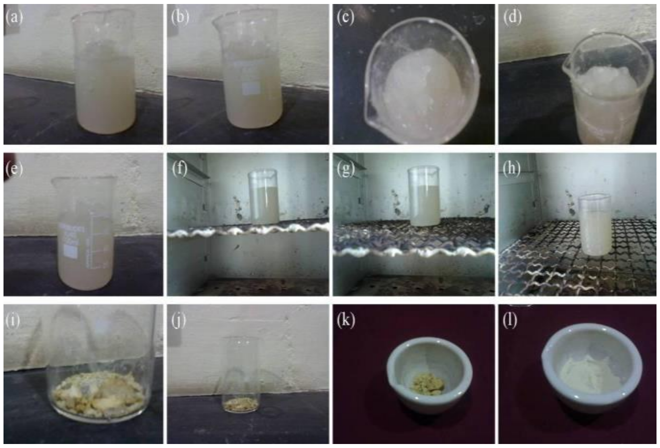

Fig. 6. Optical images of a typical piece of heat treated rice husk ash. The macroscopic morphology is maintained after the heat treatment, while the removal of organics makes the residue silica fragile and loose.

Molecular vibrational functional study was carried out by Brukker-IFS–FTIR spectrometer and the NSi particles vibrational modes. The photoluminescence (PL) properties of the products were investigated at RT under excitation wavelength at 320 nm light from He–Cd laser. The morphology of NSi samples was detected by scanning electron microscopy (JSM-5600 LV, JEOL). The stoichiometries of the nanosilica samples were investigated by SEM.

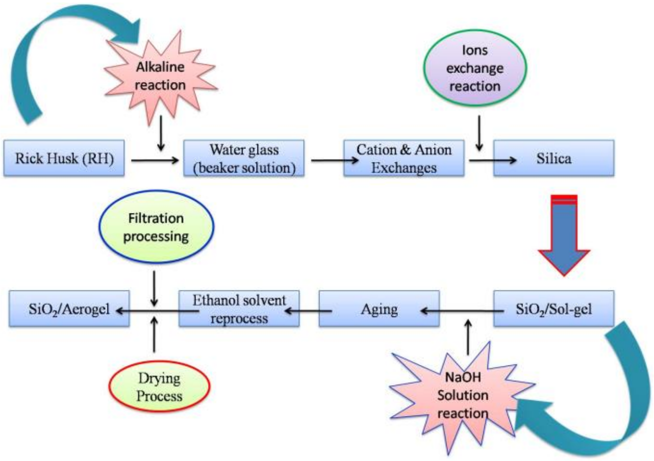

Fig. 7. Schematic diagram of a typical reaction pattern of nanosilica rice husk ash.

The morphology and microstructure were examined using transmission electron microscopy (TEM) performed on a (Philips CM12) with an acceleration voltage of 200 kV. The electrochemical responses were measured using single compartment three electrode cell setup CHI-760C, USA Potentiostat workstation. The Pt wire and Hg/HgCl$_2$ (calomel electrode) are used as counter and reference electrode, and glassy carbon electrode (GCE) as working electrode and all the potentials were measured vs GCE. The cyclic voltammetry is the most sensitive technique; to detect the trace level impurities in the measurement.

Results and discussion

XRD phase analysis

The X-ray spectra and characteristic absorption peak of silica is shown in **Fig. 8**. According to the XRD graph, the ash was mainly in an amorphous form as indicated by the broad peak on 2θ angle of 22°. The major reflections or peaks of crystalline quartz from ICSD powder diffraction files (PDF) occur at Bragg 2θ angles of 20.85°, 26.63° and 36.54°. It can be seen that no defined peaks corresponding to these Bragg 2θ angles as shown in **Fig. 8**. A rather broad peak spanning 2θ angle range of 18-30^0 which is characteristic of amorphous structures is observed. It has been reported the RH obtained by pyrolysis technique is pressed in as amorphous form which displays an atomic arrangement that is either random or has very short range order. In order to characterize the crystallinity, the crystallinity index (C$_{rl}$), was determined based on the reflected intensity data using the following the method.

$$C_{rl}\ (\%) = I_{002} - I_{am} \times 100/I_{002} \tag{3}$$

where, I$_{002}$ is the maximum intensity of (002) lattice diffraction peak and I$_{am}$ is the intensity scattered by the amorphous phase observed at the lowest intensity at a 2θ = 22° respectively.

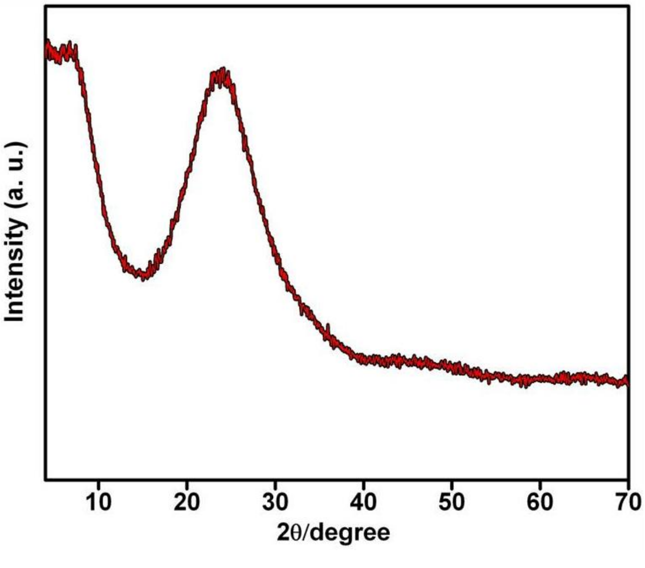

Fig. 8. XRD pattern of nanosilica rice husk ash.

FTIR analysis

The sample for IR analysis was prepared by mixing KBr pellets with 10 wt% silica powders. The resulting spectra are in **Fig. 9**. It is seen from the spectra shows that the strong bands are 466, 501 and 1091 cm^{-1}. These peaks correspond to those observed in commercial grade silica powder [**121**]. The preliminary absorption band at 1091 cm^{-1} is due to the Si-O-Si asymmetry stretching vibration. The bands at 501cm^{-1} and 466 cm^{-1} are due to the

Si-O symmetry stretching and bending vibrations respectively [**122**]. Additionally, the peak at 3493cm^{-1} is due to SiO-H asymmetry stretching vibrational mode and a peak at 1644 cm^{-1} is due to the H-O-H bending vibration, these bands result from silanol -OH groups and water bound to the silica surface by hydrogen (H) bonding. The breadth and height of O-H and Si-O bands in the rice husk (RH) samples are much smaller than that of alkali-extracted silica samples. The bending is due to the compact agglomerate of silica particles produced by the gelation reaction that leads to the increased strength of intermolecular H bonding [**123**].

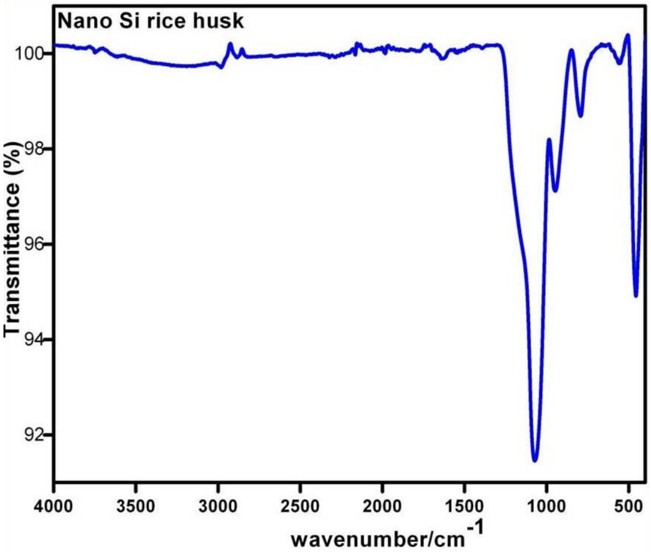

Fig. 9. FTIR spectrum of nanosilica rice husk ash.

UV-vis-NIR spectral analysis

The absorption spectrum of the nano silica sample is shown in **Fig. 10**. The energy band gap of the sample was estimated using Tauc's relationship:

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \qquad (4)$$

where, α is the absorption coefficient, hυ is the photon energy and E_g is the band gap n=1/2 for the indirect allowed transition. The energy band gap is measured with the help of absorption spectra and a graph of $(\alpha h\upsilon)^2$ vs hυ can be plotted [**124**]. The extrapolation of the straight line to $(\alpha h\upsilon)^2 = 0$ gives the value of energy band gap of the nanosilica. The energy band gap of nanosilica sample was found to be 3.8 eV. For the indirect allowed transition, n=2 and for direct forbidden n=3/2. To determine the possible transition $(\alpha h\upsilon)^{1/n}$ (υs) hυ were plotted and the corresponding band gap was obtained from extrapolating the straight portion of the graph on hυ axis [**125**]. The direct band gap calculated from $(\alpha h\upsilon)^2$ vs (hυ) plot is 3.8 eV and the indirect band gap calculated from $(\alpha h\upsilon)^2$ vs (hυ) plot is 3.23 eV as shown in **Fig. 10** (inset). The calculated values are slightly higher than that of the values for bulk material [**126**]. The increment of the values of optical band gap arises due to the improvement in the crystallinity of nanosilica. The difference in band gap of nanosilica originates from nano-stiohioemetric composition and may strongly depend on the synthesis process. In fact, the presence of silica interstitial Si ions gives rise to defect states and these may be some finite transitions probabilities from these states, which leach to indirect transitions in this material. The absorption measurement for the nanosilica sample had shown slightly higher direct and indirect values of band gap as 3.8 eV and 3.23 eV respectively.

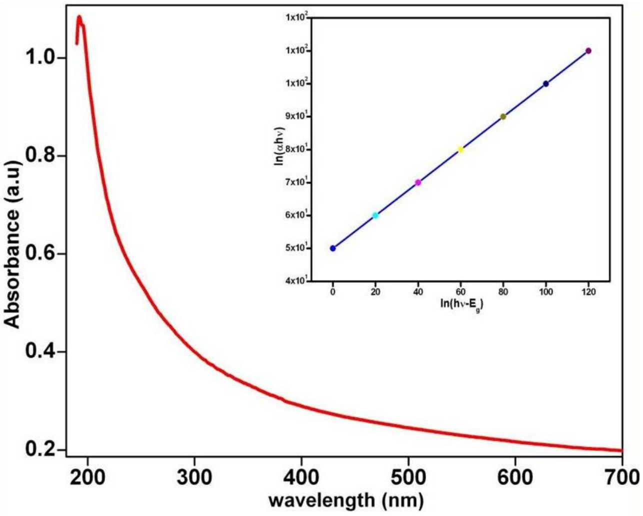

Fig. 10. UV-vis-NIR spectrum of nanosilica rice husk ash.

Surface morphological analysis

Fig. (11, 12) shows the SEM & TEM micrographs of *NSi* powder samples. The surface analysis clearly indicates that the silica is primarily in the tough epidermis of the rice husk and also filling in the spaces between the epidermal cells [**127**]. Accordingly, the structure of *NSi* shows silica fiber longitudinally aligned in a matrix consisting mainly of cellulose hemicelluloses and lignin. The image also shows a corrugated structure with useful organized epidermis on the outside of the ash. Additionally, the silica content is high on the external face of the husk, weak on the internal face and practically nonexistent with the husk. The nanosilica occurs mainly on the external face of the husk and in a laser concentration on the inner surface. A similar trend was observed in the nanosilica sample synthesized by us using a corn-cub appearance [**128, 129**]. The lamellar and the porous structure found in the TEM micrographs may be due to the oxidation of the organic compounds released during combustion.

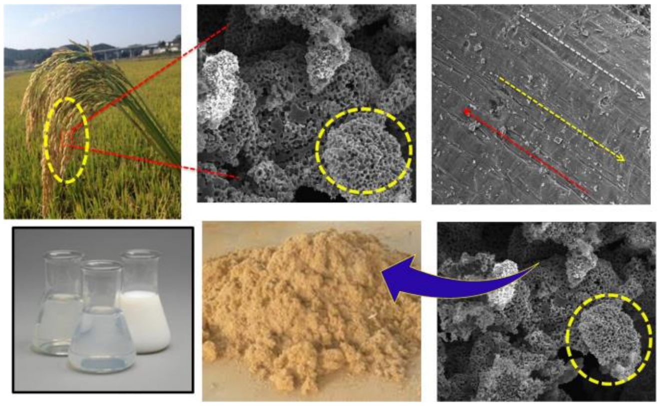

Fig. 11. SEM images of nanosilica from rice husk ash.

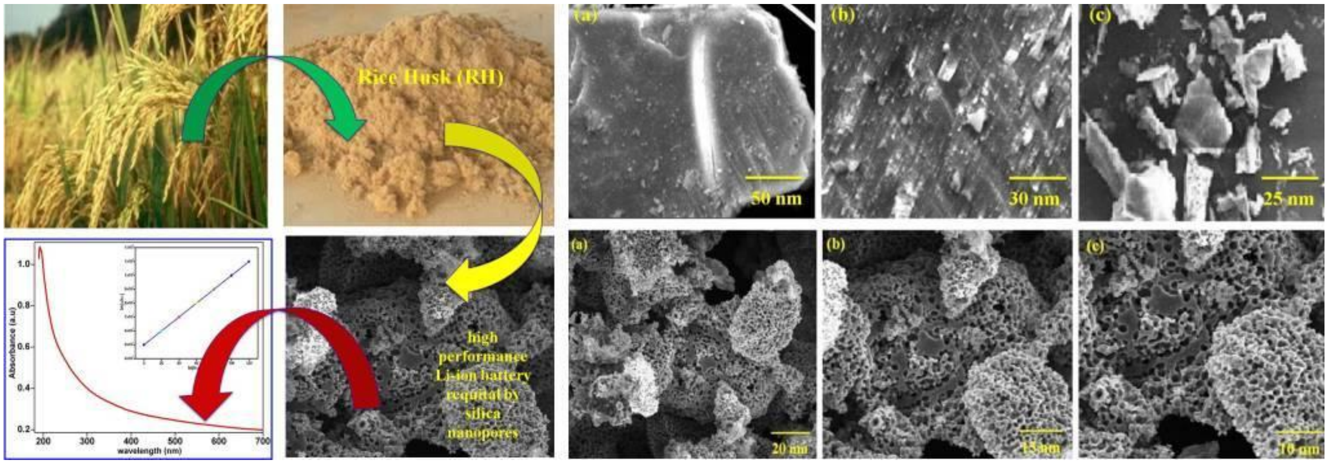

Fig. 12. (a-c serial) TEM electron micrographs of nanosilica from RHA.

Photoluminescence studies

The PL spectra of the as-obtained *NSi* are shown in **Fig. 13**. The *NSi* displayed strong blue light emission at 367 nm (3.37 eV), 446 nm (2.78 eV) and 449 nm (2.76 eV), [**130-132**]. The red emission band has a relatively constant intensity, and a red-shift of about 18 nm, while the green emission band becomes weaker compared to the red ones, and shows a blue-shift of about 14 nm. The average diameter of nano whiskers increases from 50 to 500 nm, corresponding to the SEM observations [**133-135**]. It is worth mentioning that, an average diameter of 50 nm is too thick to show any distinct quantum effect on PL. Thus the relatively small shift in emission peaks should not be directly related to size reduction. Furthermore, the *NSi* shows higher peak intensity, indicating that the *NSi* whiskers have a better light emission performance. It is believed that the more excellent light emission property of the *NSi* whiskers is ascribed to the high length/diameter aspect ratio and large amounts of stacking faults of one-dimensional structure [**136**].

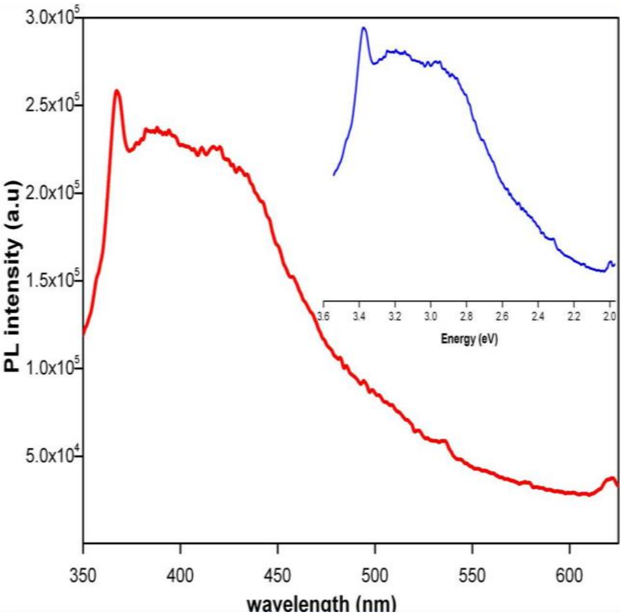

Fig. 13. Photoluminescence spectrum of nanosilica rice husk ash.

Electrochemical behavior of nano-Si from RHA

Electrochemical experiments were completed using CHI-760c, USA Potentiostat with a three electrode single compartment cell setup. The Pt wire and Hg/$HgCl_2$ are used as counter and reference electrode, and glassy carbon electrode (GCE) as working electrode and all the potentials were measured vs. GCE. The preparation of the modified electrode is very important in electrochemistry because the electrochemical measurement is one of the most sensitive techniques and trace amounts of impurities may show up in this measurement. The glassy carbon electrode surface was polished using 0.5 μm alumina slurry, followed by extensive washing with distilled water. For the preparation of SiO_2 modified GCE (SiO_2/GCE), sample amount of 1-2 mg were placed on micro slide, making wet with ethanol and rubbed over the material, causing some amount of SiO_2 adhere to the electrode surface when dried [**137-139**]. All solutions were purged with purified N_2 gas for about 10 minutes before doing measurements. Unlike bulk Si, the recovered nano-Si has high functionality due to this small size and porous nature. The electrochemical responses of the SiO_2/GCE were studied using cyclic voltammogram (CV) in 0.1 M Phosphate Buffer (PBS) as electrolyte (pH 7.0) at a scan rate 50 mV/s in the potential range -1.5 V to +1.5V [**140, 141**]. **Fig. 14** shows three peaks in the first scanning cycle; the redox response observed at -1.15 V and -0.75V is due to the cathodic reduction of SiO_2 and the anodic oxidation of silicon, respectively. Clearly the reduction of SiO_2 starts approximately at -1.0 V *vs.* SiO_2/GCE electrode and the irreversible anodic response observed at +0.87 V. This proves the nano-Si has a high level of functionality due to its small size, porous nature and higher electrochemical activity without any modification [**142**]. Additionally, the cycling stability is excellent as well. An activation process occurred over the first few cycles, as indicated by the increase of the CV peak intensity and a decrease of the charge transfer resistance measured by impedance spectroscopy [**143, 144**]. From the second cycle, the broad peak disappeared with gradually evolve quasi-reversible response at -1.40 V after shifted towards cathodic region 25 mV (insert). The increase of the cathodic current with decrease the anodic current in subsequent cycles at +0.87 V by the adsorption of solid interfacial layer on the SiO_2/GCE after decomposition with electrolyte indicated in the insert figure. From this CV scanning performance of rice husks reveals that it is a potential source for silica that could be used in the future application such as rechargeable battery (lithium ion) and solar grade silicon [**145-148**].

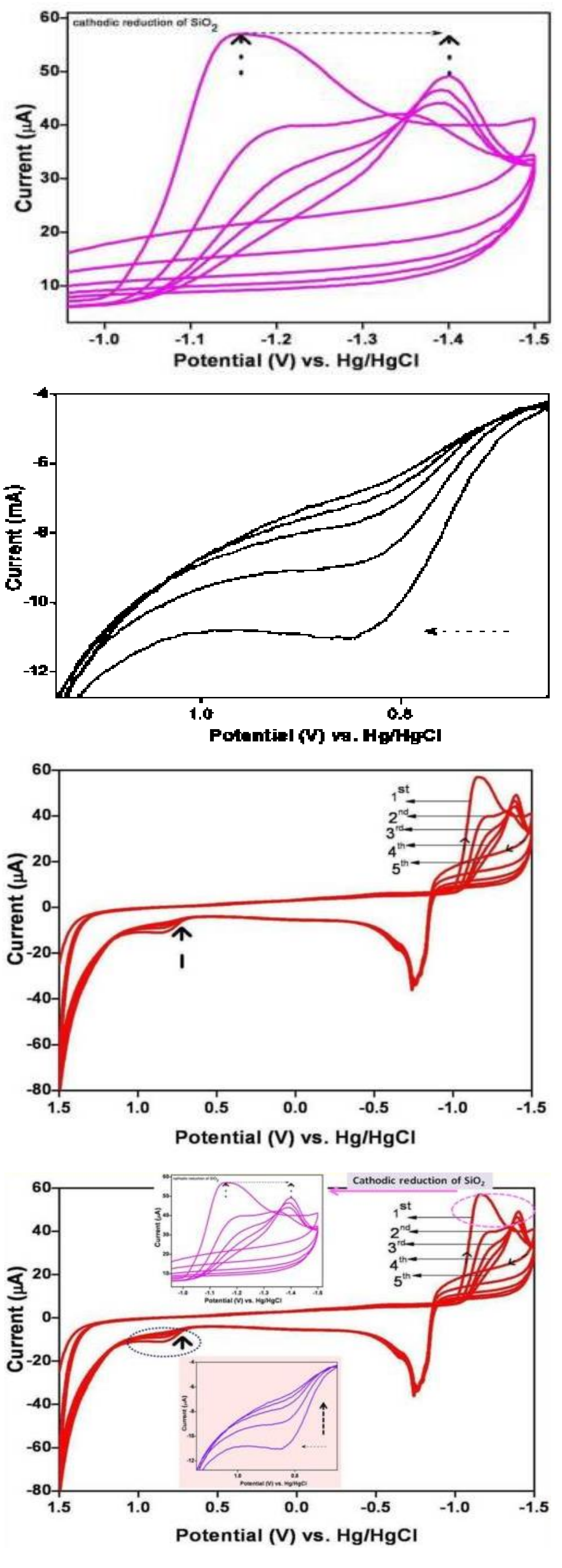

Fig. 14. Electrochemical behavior of nanosilica rice husk ash.

Conclusion

In summary, whereas silicon nanomaterials have found potential application in a number of areas, green, cost-effective, and scalable syntheses of them from sustainable sources still remains challenging. To conquer this barrier, we developed a simple route of recovering nano-Si directly from rice husks, an agricultural waste, in which silicon naturally exists in the form of silica nanoparticles. By utilizing the strongly exothermic reactions, we succeeded in preserving the nanostructure form of silicon. Nanosilica was successfully synthesized from rice husk via simple modified sol-gel method at RT. The XRD studies revealed the formation of *NSi* with particle sizes vary from 70 to 140 nm. FTIR study confirms the presence of Si-O, C=C, C=O, O-H and C-H bonds. The formation mechanism of nanosilica structure was investigated by TEM observations. Hence it is reasonable to expect that this simple approach can easily be scaled up to prepare nanosilica structures for important applications in the large field of nanotechnology. Our study identified that rice husk can be used for the production of valuable and widely applicable nanoscale silica. This presents a green source of silica that solves disposal and pollution problems.

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