Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (4): 1218-1226

(International Peer Reviewed Journal)

One-Step Synthesis of Silica Nanoparticles by Thermolysis of Rice Husk Ash Using Non Toxic Chemicals Ethanol and Polyethylene Glycol

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Accepted on 10th July 2015

ABSTRACT

Amorphous silica nanoparticles were synthesized by injection of rice husk ash (RHA) silica diluted in ethanol into hot polyethylene glycol (PEG) solution at 180 °C and allowing the mixture for 2 h at 80 °C. The obtained product was characterized by X-ray diffraction (XRD), Fourier Transform Infrared spectra (FTIR) and transmission electron microscope (TEM). The results indicated that the amorphous structure of silica nanoparticles were successfully formed having well defined and regular spherical shape. TEM exhibits high concentrated particles with a size in the range of 65 to 70 nm whereas some few particles are peculiarly large. With this exception which induces an unexpected broad particle size distribution, the optical properties UV-vis absorption and photo luminescence of the obtained silica are in good agreement with those of previous conventional preparation techniques.

Keywords: Rice husk ash, thermolysis, nano silica, non toxic chemicals.

INTRODUCTION

Silica is one of the white minerals along with china clay, talc and calcium carbonate abundantly used in industries. World demand for silica in its diverse forms encompassing precipitated silica, fumed silica, silica gel and silica sol will rise 6.3 % /year to 2.7 million metric tons in 2014 [1], the main ones being the glass, foundries, construction, ceramics, and the chemical industry as catalysts, support for biomedical applications such as drug's delivery, additive for plastics or filler for concrete and other construction composites [2-5]. Silica nanoparticles have received great deal of research because of their interesting properties associated to their stability, low toxicity and ability to be functionalized with a range of molecules and polymers. These properties depend essentially to the structure which is inseparably to the synthesis process and raw materials used. One of the most referred is amorphous nano silica which is obviously the phase of synthesis product dissimilar to the crystalline found in nature [6-8]. Many reports have shown successful synthesis of amorphous nano silica either pure or doped in the form of composites and thin films. Precursors used are often organic compounds such as tetraethylorthosilicate (TMOS), tetraethylorthosilicate (TEOS) or polyethoxydisiloxane (PEDS) and inorganic systems like sodium silicate

and olivine. A variety of synthesis processes are described in the literature including sol-gel [5, 8-9], micro emulsion [7, 11-12], microwave-assisted acid catalyst [12-14] and vapour techniques [15-17]. Recently greener methods which avoid the use of hazard precursors have been reported [ref]. These routes use natural starting materials such as corn cop [9], sugar cane bagasse, coffee husk, [18-19], wheat husk [20], and rice husk [21-26]. Rice husk is a an agricultural waste from rice mill, it is composed of 15 - 20 wt.% SiO_2, 74 wt.% of organic part (composed of cellulose, lignin and hemicellulos, the latter is a mixture of D-xylose, L-arabinose, methylglucoronic acid and D-galactose and 4 wt.% of ($A1_2O_3$ + Fe_2O_3 + Ca O + Mg O) [27-29]. It is a good alternative to the conventional materials and has a great potential as a bio-source for large scale production since it is largely available. When calcinated under controlled conditions: oxidation condition (air or best oxygen), 600-700°C from 1-4 h, rice husk leads to the formation of rice husk ash (RHA) consisting of 61-71 wt. % silica and 36 wt.% of unburnt carbon and others impurities [30-31].

Subsequently various procedures have been developed to convert RHA to silica: fluidized bed [20], chemical pre and post treatment using acid and base solution [2], pressurized hot water treatment processes [21], carbonization and combustion [22], non isothermal decomposition in oxidizing atmosphere [23]. However, alkaline dissolution of RHA to sodium/potassium silicate solution, which can easily be transformed to silica by aforementioned techniques, found to likely a most yielding method to date with most than 93- 98 % purity [32-35].

More attention has been paid to refine the quality of product with a regard of carefully control by the morphology, particle size and size distribution, and structure or surface properties such as specific surface area. Initially it was Stöber and co-workers who obtained through hydrolysis in strong basic medium monodisperded and non-porous silica particles [36]. There has been considerable progress made in the synthesis of silica and more recently, by control pH and ratio of the water-to-surfactant molar, various mesoporous structures with relatively higher specific surface area have been tailored [37].

There are still efforts to develop cost-effective techniques to synthesize and process nano silica that can meet major challenges with regards to collection, uniformity, and reproducibility for concrete applications. Hence, the objective of our work is to extract amorphous silica from rice husk ash, using a thermolysis route. This method has a dual benefit, valuable silica particles at lower cost can be produced with reducing disposal as well as pollution challenges.

MATERIALS AND METHODS

We used rice husk from a rice mill in Maroua, Far North Region of Cameroon. The sample was washed in water to remove adhering soil and sand which easily settles down. The important part remained in suspension is recovered with sieve (400 µm) and wringed. After drying in an oven (Type Scientific, series 2000) at 110°C for 24 h, the obtained proper rice husk was burned at 700 °C in a muffle furnace, with 5 °C min^{-1} for the heating rate and 2 h at the peak temperature. This firing program was found to be an optimum, according to previous work investigated on the calcination of rice husk, a temperature of 800°C is the maximum to obtain chemically reactive amorphous silica from RH. At higher temperature crystalline phases such as cristobalite will be formed while below 500 °C, there is incomplete carbonization [38-39]. The obtained white fibrous ash was then put in water (5.0 g of ash for 50 mL of deionized water), the mixture was stirred for 2 h and filtered with Whatman paper no 41. The residue which is considered as clean rice husk ash, named RHA, was used for further experiments. To investigate the effect of this washing step, microstructure analyses were performed on rice husk ash before and after the washing using a "A Zeiss Ultra Plus FEG Scanning Electron Microscopy (SEM) was used for surface morphology analysis, equipped with an Oxford detector EDX at 20 kV which uses Aztec software for elemental analysis".

Others materials used are deionized water, ethanol 95 % v/v and polyethylene glycol 400 (PEG 400), all the chemicals were used as received from Supplied Laboratory & Analytical Supplies (PTY) Ltd.

The synthesis of nano silica was performed by the hot injection method [40-41]. 3.0g of RHA was dispersed in 20 g of ethanol used as dispersing agent; the solution was then heated at 50 °C and vigorously stirred for 10 min to obtain the precursor solution. It was then rapidly injected into PEG, the capping agent which was previously heated at 180 °C under reflux. The temperature was then adjusted at 80 °C and held for 2 h. Finally, the solution was allowed to cool at room temperature, the silica was precipitated by adding 10 mL of ethanol and centrifuged then mixed and washed with the same solvent.

The as prepared sample was analysed on the Transmission electron microscopy (JEOL 1010 TEM) with accelerating voltage of 100 kV, Megaview III camera, and Soft Imaging Systems TEM software and the High Resolution Transmission Electron Microscope with an accelerating voltage of 200 kV (JEOL 2010 HRTEM) to verify the particles morphology, size and size distribution. The phase composition was investigated by Fourier Transform Infrared spectra recorded in the range of 200–3000 cm^{-1} using Bruker FT-IR Tensor 27 spectrophotometer and by X Ray Diffraction (XRD). Powder diffraction patterns were recorded in the high angle 2 theta range (5–70°) using a Bruker AXS D8 diffractometer equipped with nickel filtered Cu-K a radiation (l = 1.5418 Å) at 40 kV, 40 mA. The scan speed and step sizes were 0.3°/min and 0.001s respectively. In addition, optical absorption measurements were carried out using a Varian Cary 50 UV-visible spectrophotometer with ethanol as reference in quartz curvets (1 cm path length). Photoluminescence was used to measure on a Perkin-Elmer LS 55 fluorescence spectrometer.

RESULTS AND DISCUSSION

Effect of washing rice husk ash before use: The contribution due to the washing of rice husk ash before use is quite distinct on the respective microstructure of the material before and after washing as seen in figure 1a and 1b. The sample before washing shows agglomerated bulk material. After washing in water, the particles appear loose yielding a more organized microstructure.

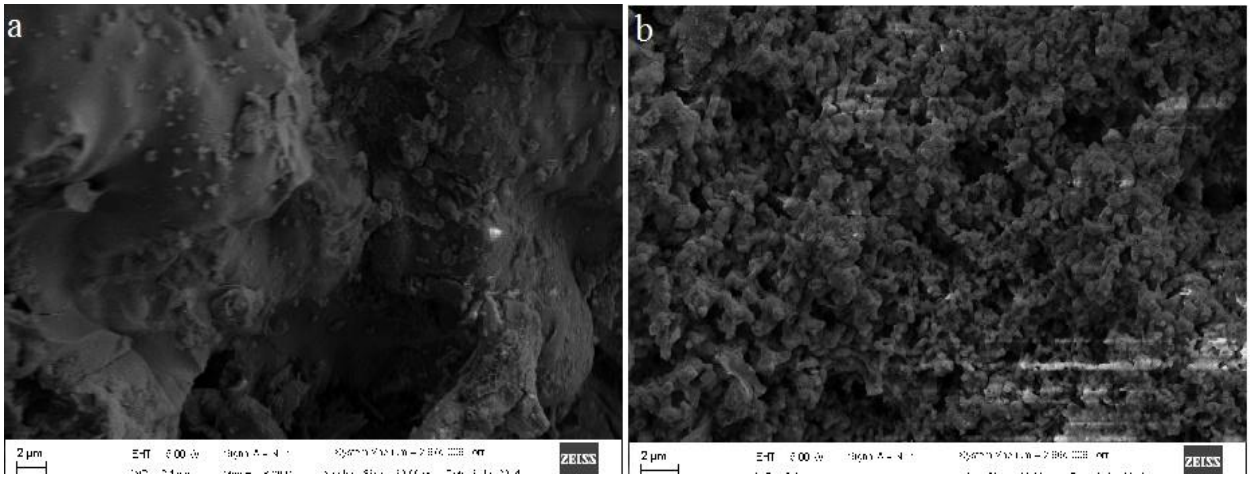

Figure 1: SEM micrographs of rice husk ash (a) before and (b) after washing in water

Structural characterization of the silica nanoparticles: The IR spectrum of the synthesized silica as shown in figure 2 is typical infrared reflection curve of silica nanoparticles as several previous studies have investigated. It displays a strong and broad absorption band peak at 447 cm^{-1} which is usually ascribed to the bending of vibration of Si-O-Si [42]. The others peaks at 797 cm^{-1} and 1056 cm^{-1} can be considered to

have shifted from 802 $cm^{-1}$and 1105 cm^{-1} corresponding to the symmetric and antisymmetric stretching vibration of Si–O respectively [43-44].

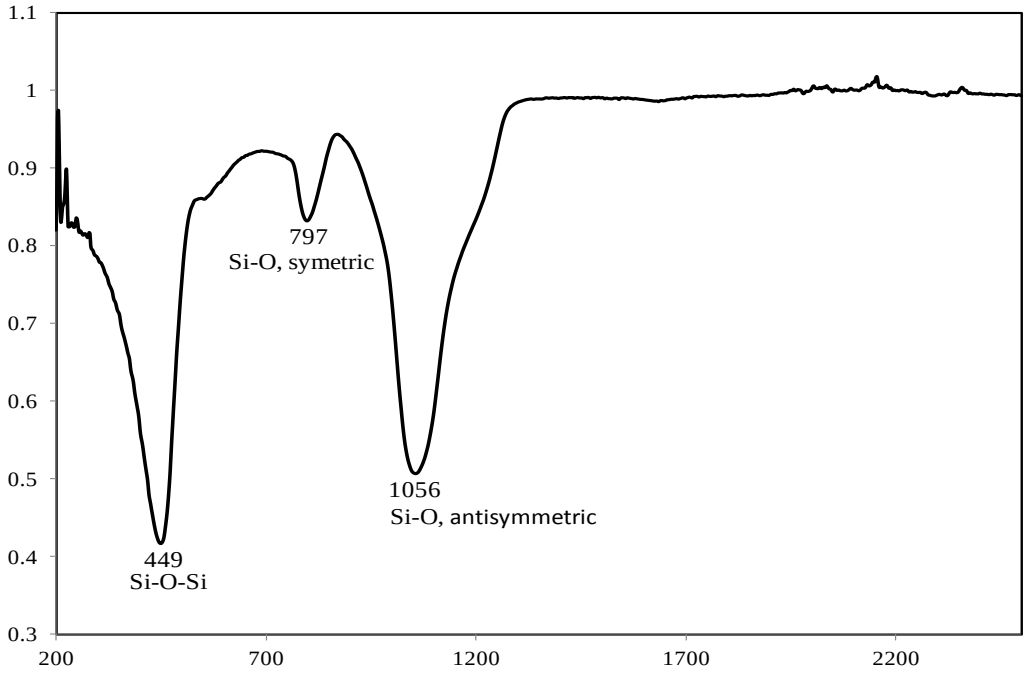

Figure 2: FTIR spectra of synthesized nano silica

Figure 3 shows X-ray powder diffraction pattern of the prepared nano silica which is characterized by a broad halo at about 2θ = 15-25 ° region which confirms the amorphous structure of the studied sample. However, some few peaks appear at 2θ = 26.22, 26.76 and 31.48, indicating the presence of a crystalline phase, which can only be attributed to a residual impurity from the raw material. Comparison with the XRD pattern of RHA shows a common peak at 2θ = 26.76 °.

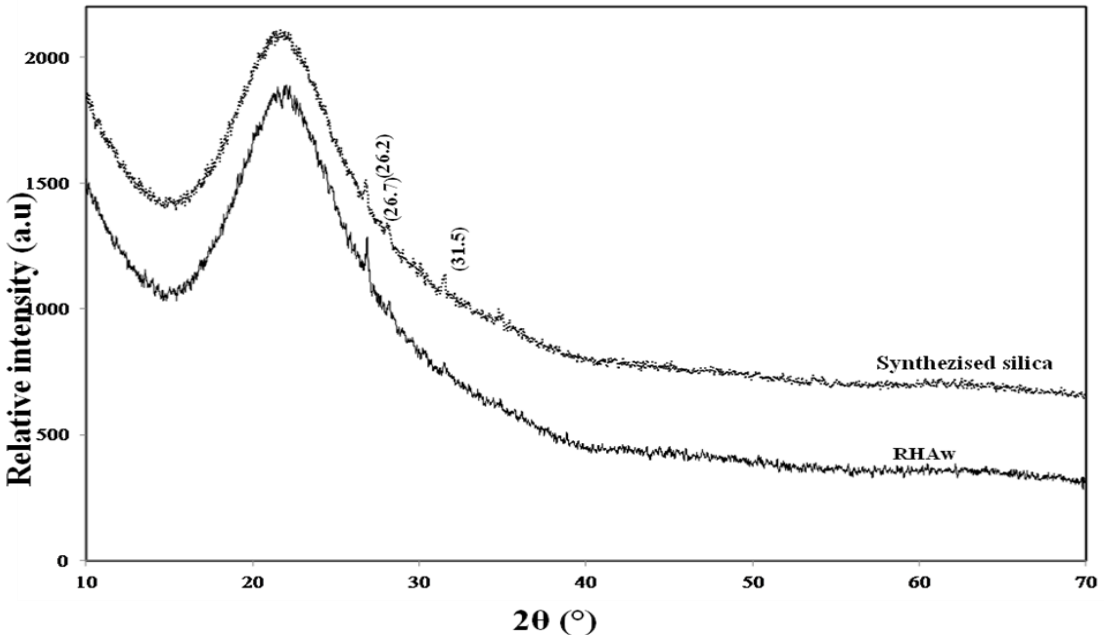

Figure 3: XRD diffractograms of rice husk ash and nanosilica

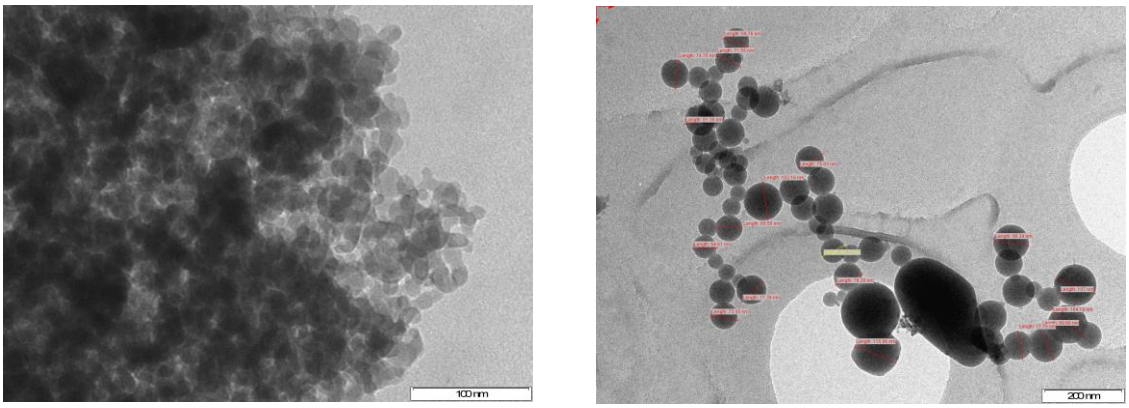

Figure 4: TEM images of nanosilica

Figure 4 shows the TEM images of the synthesized silica. The particles are dispersed, having well defined, regular, spherical shape. There is however a heterogeneity concerning their size, with the majority of particles in the 60-70 nm size range and some larger particles in the 105-112 nm range.

Optical characterization of silica nanoparticles: As illustration of optical properties, Figure 5 and 6 present respectively the UV-visible (UV-vis) absorption and the photoluminescence (PL) emission spectra nanosilica solution. The UV-vis spectrum reveals an absorption band edge at 350 nm, whereas the PL spectrum displays a blue band centred at 423 nm spawned by 350 nm excitation. This excitation was chosen on the base result obtained by Vaccaro et al [45] according to which the 354 nm is the one of the 02 excitations peaks that induce the higher PL amplitude, the other one at 240 nm gives lower amplitude but still in the same edge since the authors have demonstrated that change of excitation from 210 to 350 nm cause variations of the PL amplitude, whereas the spectral features are poorly influenced. These optical features are similar to those obtained in previous reports and attributed to Si-O-Si bond confirming the presence of silica nanoparticles [45- 47].

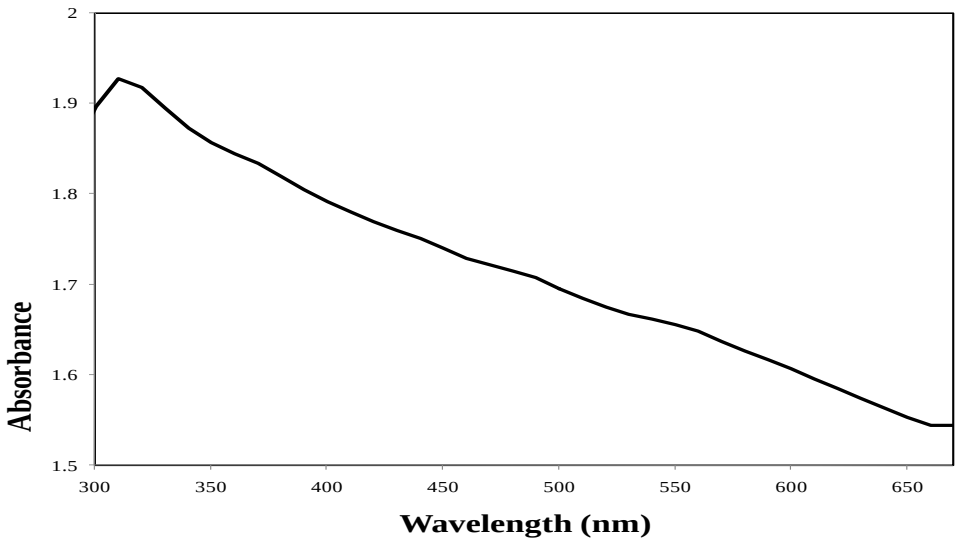

Figure 5: UV–vis absorption spectrum of nanosilica solution

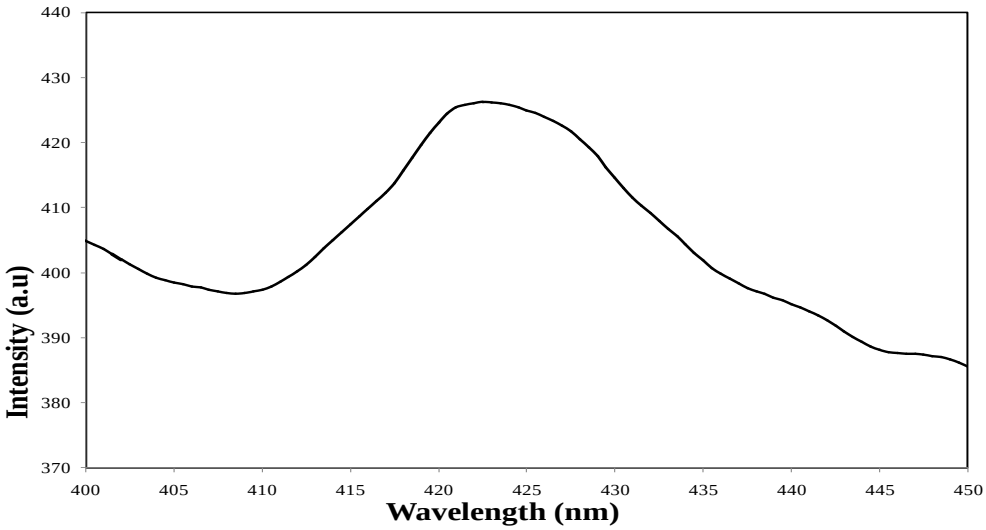

Figure 6: Photoluminescence spectrum of nanosilica solution

We used the widely available polyethylene glycol (PEG) and ethanol respectively as solvents to transform silica from RHA through a thermolysis route. This is an efficient and highly explored technique that has been used as an alternative to conventional for nanoparticle synthesis. RHA particles diluted in ethanol, when injected into hot solution of PGE at 180 °C lead to the instantaneous formation of silica nuclei and a drop in temperature to 80 °C prevents the formation of new nuclei since the energy barrier for nucleation cannot be overcome and the growth process is favoured while further nucleation is suppressed. Nuclei were allowed to grow for 2 h at 80 °C, these were predicted optimum conditions to balance the surface roughening due to rapid growth at the initial period and the surface degradation induced at high temperature growth temperature [48]. Furthermore, PEG as stabilizing agent was supposed to prevent the formation of agglomeration of formed nanoparticles. Our results showed a high concentration of particles with size between 65 and 70 nm, and also few peculiar agglomerated particles with size up to 112 nm. With this exception which consists of the occurrence of unexpected growth of some particles, all other properties of the obtained silica are in good agreement with the previous conventional preparation techniques.

CONCLUSIONS

We have shown that it is possible to obtain silica nanoparticles from agro waste rice husk using harmless and widely available polyethylene glycol (PEG) and ethanol. The advantages of this facile and environmentally friendly method is its mechanism which spawns a homogeneous nucleation at the earlier age even though the next step concerning the growth is still a challenge to control. The route could be used for the large scale industrial synthesis of silica nanoparticles.

ACKNOWLEDGMENTS

The research was carried out with the financial support of the TWAS in the frame of Fellowship for Research and Advanced Training, 2014. The authors also wish to express their heartfelt gratitude to Professor John Simonis, Department of Hydrology, University of Zululand, Rep of South Africa for his assistance in conducting the firing.

REFERENCES

[1] Flörke, Otto W. et al, **2008** "Silica" in *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH. doi:10.1002/14356007.a23_583.pub3.
[2] Iler, R. K. **1979**, *The Chemistry of Silica*,Plenum Press, ISBN 0-471-02404-X.

[3] T. Heikkil, J. Salonen, J. Tuura, M.S. Hamdy, G. Mul, N. Kumar, T. Salmi, D.Yu. Murzin, L. Laitinen, A.M. Kaukonen, J. Hirvonen, V.-P. Lehto, Pharmaceutical Nanotechnology: Mesoporous silica material TUD-1 as a drug delivery system, *International Journal of Pharmaceutics*, **2007,** 331, 133–138, doi:10.1016/j.ijpharm.2006.09.019.
[4] N.Vijayarethinam, "Silica Fume Applications," *World Cement*, **2009,** 40, 97-100.
[5] B. Gorji, M.R. Allahgholi Ghasri, R. Fazaeli, N. Niksirat, Synthesis and Characterizations of Silica Nanoparticles by a New Sol-Gel Method, *Journal of Applied Chemical Research*, **2012**, 6(3), 22-26.
[6] R. S. Kumar, M. Vinjamur, and M. Mukhopadhyay, A Simple Process to Prepare Silica Aerogel Microparticles from Rice Husk Ash, *International Journal of Chemical Engineering and Applications*, **2013**, 4(5), 321-325.
[7] Tzong-Horng Liou, Chun-Chen Yang, Synthesis and surface characteristics of nanosilica produced from alkali-extracted rice husk ash, *Materials Science and Engineering B,* **2011,** 176, 521–529, doi:10.1016/j.mseb.2011.01.007
[8] B. Gorji 1, M.R. Allahgholi Ghasri, R. Fazaeli, N. Niksirat, Synthesis and Characterizations of Silica Nanoparticles by a New Sol-Gel Method, *Journal of Applied Chemical Research*, **2012,** 6(3), 22-26.
[9] E. A. Okoronkwo, P. E. Imoisili, S.O.O. Olusunle, Extraction and characterization of Amorphous Silica from Corn Cob Ash by Sol-Gel Method, *Chemistry and Materials Research*, **2013**, 3(4), 68-73.
[10] V Ganesh Aditya, Bikash Ranjan Mallick, preparation of silica nanoparticles using microemulsion techniques, *Thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Technology*, Department of Chemical Engineering National Institute of Technology Rourkela, **2008.**
[11] A. B. D Nandiyanto; S. G. Kim, F. Iskandar, K. Okuyama, "Synthesis of spherical mesoporous silica nanoparticles with nanometer-size controllable pores and outer diameters", *Microporous and Mesoporous Materials*, **2009,** 120 (3), 447.doi:10.1016/j.micromeso.2008.12.019.
[12] Derek D. Lovingood, Jeffrey R. Owens, Michael Seeber, Konstantin G. Kornev, Igor Luzinov, Preparation of Silica Nanoparticles Through Microwave-assisted Acid-catalysis, *Journal of Visualized Experiments*, DOI: doi:10.3791/51022
[13] Si-Han Wu, Chung-Yuan Mou, and Hong-Ping Lin, Synthesis of mesoporous silica nanoparticles, *Chem. Soc. Rev.,* **2013**, 42, 3862-3875, DOI: 10.1039/c3cs35405a.
[14] Monde Qhobosheane, Swadeshmukul Santra, Peng Zhang and Weihong Tan, Biochemically functionalized silica nanoparticles, *Analyst*, **2001**, 126, 1274–1278, DOI: 10.1039/b101489g.
[15] Yongchun Chen, Shuxue Zhou, Haihua Yang, Limin Wu, Structure and Properties of Polyurethane/NanosilicaComposites, Wiley InterScience, 1032-1039, DOI 10.1002/app.21180.
[16] M. F. Zawrah,A. A. El-Kheshen and Haitham M. Abd-el-Aal, Facile and economic synthesis of silica nanoparticles, *Journal of Ovonic Research*, **2009**, 5(5), 129-133.
[17] Thangaraja Amirthalingam, Jegatheesan Kalirajan and Arunkumar Chockalingam, Use of Silica-Gold Core Shell Structured Nanoparticles for Targeted Drug Delivery System, Nanomedic Nanotechnol 2:119. doi:10.4172/2157-7439.1000119.
[18] Affandi S, Setyawan H, Winardi S, Purwanto A, and Balgis R "A Facile Method for the Production of High Purity Silica Xerogels from Bagasse Ash, *J. Adv. Powder Tech.,* **2009**, 20, 468-472.
[19] Espindola-Gonzalez A, Martinez-Hernadez AL, Angeles-Chavez C,Castano VM, Velasco-Santos C Novel Crystalline SiO2 Nanoparticles via Annelids Bioprocessing of Agro-Industrial Wastes, *Nanoscale Res Lett.,* **2010,** 5,1408–1417
[20] S. H.Javed, F. H.Shah, M. Manasha, Extraction of amorphous silica from wheat husk using $KMnO_4$. JFET, **2011,** 18, 39-46.
[21] Sy-Thang Ho, Quang-Khieu Dinh, Thai-Hoa Tran, Huu-Phu Nguyen and Thanh-Dinh Nguyen, One-Step Synthesis of Ordered Sn-Substituted SBA-16 Mesoporous Materials Using Prepared

Silica Source of Rice Husk and Their Selectively Catalytic Activity, *The Canadian Journal of Chemical Engineering,* **2013**, 91, 35-46.

[22] L. Sun, K. Gong, "Review, silicon-based materials from rice husks and theirs applications*", Ind. Eng. Chem. Res.,* **2001,** 40, 5861–5877

[23] D. Singh, R. Kumar, A. Kumar, K. N. Rai, Synthesis and characterization of rice husk silica, silica-carbon composite and H_3PO_4 activated silica, *Cerâmica,* **2008,** 54,203-212.

[24] Van Hai Le, Chi Nhan Ha Thuc and Huy Ha Thuc, Synthesis of silica nanoparticles from Vietnamese rice husk by sol – gel method, *Nanoscale Research Letters,* **2013.**

[25] Ram Prasad, Monika Pandey, "Rice Husk Ash as a Renewable Source for the Production of Value Added Silica Gel and its Application: An Overview". *Bulletin of Chemical Reaction Engineering & Catalysis,* **2012,** 7 (1), 1-25.

[26] S.Chandrasekhar, K.G. Satyanarayana, P.N. Pramada, P. Raghavan, Review Processing, properties and applications of reactive silica from rice husk an overview, *J. Mat. Sci.*, **2003,** 38: 3159–3168.

[27] N.K.Sharma, W.S. Williams, A. Zangvil, Formation and structure of silico carbide whiskers from rice hulls, *J. Am. Ceram. Soc.*, **1984,** 67, 715-720.

[28] Tang, Qi. and Wang Tao. Preparation of silica aero-gel from rice hull ash by supercritical carbon dioxide drying. *J. Supercritical Fluids,* **2005,** 35, 91–94.

[29] R.V. Krishnarao, M.M. Godkhindi, Distribution of silica in rice husks and its effect on the formation of silicon carbide. *Ceram. Int.*, **1992,** 18, 243-249.

[30] U. Kalapathy, A. Proctor, J. Schultz, A simple method for production of pure silica from rice hull ash. Biores. Tech. **2000,** 73, 257–262.

[31] V.R. Shelke, S.S Bhagade, S.A.Mandavgane, Mesoporous Silica from Rice Husk Ash. *Bull. Chem. React. Eng. Catal.*, **2010,** 5(2), 63–67.

[32] J. P. Nayak and J. Bera, Preparation of Silica Aerogel by Ambient Pressure Drying Process using Rice Husk Ash as Raw Material, Trans. Ind. Ceram. Soc, **2009,** 68 (2) 1-4.

[33] R. S. Kumar, M. Vinjamur, and M. Mukhopadhyay, A Simple Process to Prepare Silica Aerogel Microparticles from Rice Husk Ash, *International Journal of Chemical Engineering and Applications,* **2013,** 4(5).

[34] R.V.Krishna Rao, J. Subrahmanyam, T.J.Kumar, Studies on the formation of black particles in rice husk silica ash. *J. Eur. Ceram. Soc.*, **2001,** 21(1), 99-104.

[35] F. J. Arriagada and, K. Osseo-Asare, Synthesis of Nanometer-Sized Silica by Controlled Hydrolysis in Reverse Micellar Systems, Chapter (Book), The Colloid Chemistry of Silica Chapter 5, pp 113–128 in Advances in Chemistry, Vol. 234, American Chemical Society.

[36] Liangming Xiong, Edson H. Sekiya, Pornapa Sujaridworakun, Shigetaka Wada and Kazuya Saito, Burning temperature dependence of rice husk sshes in structure and property, *Journal of Metals, Materials and Minerals,* **2009,** 19(2), 95-99.

[37] Ezzat Rafiee, Shabnam Shahebrahimi, Mostafa Feyzi and Mahdi Shaterzadeh, Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material), *International Nano Letters*, **2012**, 2, 29, 1-8.

[38] Jan-Jezreel F. Saceda and Rizalinda L. de Leon, properties of silica from rice husk and rice husk ash and their utilization for zeolite y synthesis, *Quim. Nova,* **2011**, 34(8), 1394-1397.

[39] S. Mahajan, Meenu Rani, R. B. Dubey and Jagrati Mahajan, Synthesis of CdSe crystal using hot injection method.

[40] C.M. Donega, P. Liljerath and D. Vanmaekel "Physicochemical evalution of hot injection method, a synthesis route for monodisperse nanocrystal" published in small in 2005. *International Journal of Latest Research in Science and Technology,* **2013**, 2(1), 518-521.

[41] xu ying-mei, qi ji, he de-min, wang dong-mei, chen hui-ying, guan jun, zhang qiu-min, preparation of amorphous silica from oil shale residue and surface modification by silane coupling agent, oil shale, **2010**, 27(1), 37–46.

[42] J. Bock, Su, G.-J., Interpretation of the infrared spectra of fused silica. *J. Amer. Ceram. Soc.,* **1970,** 53, 69.

[43] Tomozawa M., Hong, J.-W., Ryu, S.-R., Infrared (IR) investigation of the structural changes of silicaglasses with fictive temperature. *J. Non-Crystall. Solids,* **2005,** 351, 1054.
[44] J.C. Philips, Structura model of Raman "defect" bands of vitreous silica. *Phys. Rev., B,* **1987,** 5, 6409.
[45] L. Vaccaro, L. Spallino, S. Agnello, G. Buscarino, and M. Cannas, Defect-related visible luminescence of silica nanoparticles, *Phys. Status Solidi C,* 14(4), 658-661.
[46] Y. D. Glinka, S Lin, Y.T. Chen, *Physical Review B,* **2002**, 66, 035404, 1-10.
[47] Alban Colder, Friedrich Huisken, Enrico Trave, Gilles Ledoux, Olivier Guillois, C´ecile Reynaud, Herbert Hofmeister and Eckhard Pippel, Strong visible photoluminescence from hollow silica nanoparticles, *Nanotechnology,* **2004,** 15 , L1–L4.
[48] C.M Donega, S.G. Hickey, SF Wuisfer, D.V Maekelbergh, Physicochemial evaluation of the hit injection method, a synthesis route for monodisperse nanaocrystals, *Small,* **2005**, 1(2), 1152-1162.

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