Synthesis and characterization of mesoporous SiO_2 nanoparticles synthesized from Biogenic Rice Husk Ash for optoelectronic applications

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Abstract. An inexpensive methodwas used to synthesize mesoporous silica (m-SiO_2) nanoparticles from sticky rice husk ash. The absence of sharp peaks in XRD pattern confirmed the amorphous nature of silica nanopowders. The SEM and TEMmicrographsof m-SiO_2reveal that the SiO_2 nanoparticles had a clustered spherical shape. The average particle size of the SiO_2 nanoparticles evaluated from TEM were observed to be 50 nm. The surface area of the silica nanopowderwere measured from BET analysis to be 7.1548 m^2g^{-1}.Thespherical silica nanoparticlecan be applied forenergy storage and optoelectronic applications.

Key words: Rice husk ash, silica nanoparticle, microstructural analysis, surface and pore areameasurements.

1. Introduction

Rice husk (RH) is a major by-productof rice milling, and is also an abundant form of agricultural waste.RH can be recycled to produce high value eco-materials, such as silicon (Si), silica (SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4) and graphene (G)[1-3]. The chemical composition (in percentage) of raw rice huskhas been reported to contain both organic (74%) and inorganic constituents (26%). The organic constituents include cellulose, hemi cellulose, lignin, L-arabinose, Methylglucuronic acid, D-galactose and some proteins and vitaminsthat can be removed from rich huskduring the burning process [4]. Theremaining majorinorganic component of rice husk ask (RHA)is SiO_2 (80%) along with some minor inorganic constituentsincluding alumina (3.93%), sulfur trioxide (0.78%), iron oxide (0.41%), calcium oxide (3.84%), magnesium oxide (0.25%), sodium oxide (0.67%), potassium oxide (1.45%), and a loss of ignition (8.56%).
Nanostructured SiO_2can be synthesized from RHAthrough chemical means (acid/alkali leaching and post heat treatment)as well as non-isothermal, fluidized bed, carbonization and combustion, pressurized hot-water, microwave hydrothermal, and precipitation [5] treatments.Of the different synthesis methods, the chemical methodconsisting ofacid leaching and postannealing is one the most simple and successful techniquesto synthesize the ultrafine SiO_2 powder[2] from RHA.Silicon dioxide or silica or SiO_2 is one of the most common materials used in optoelectronic applications. It has a wide bandgap (~9 eV)that results in a high native transparency that extends from infrared to UV [6, 7]. Fe_2O_3-doped silica nano-spheres have been used in magnetic targeting [8], and SiO_2 nanoparticles are functionalized with different receptors including naphthalimide,BODIPY, andazobenzene for

chemosensor applications to detect lead (Pb^{2+}) and mercury (Hg^{2+}) heavy metals in drinking water [9-11]. For energy storages, the small particle size and high surface area allows for SiO_2-carbon (SiO_2-C)nanocompositesto be used as the anode electrodeof lithium ion batteriesin order to provide a long cycling life and a high, reversible capacity (485 $mAhg^{-1}$)[12].

The objective of this research work is to synthesize bio-genicmesoporous silica nanoparticlesfrom sticky rice husk ash. The microstructural, elemental compositions, functionality, and the porosity of nanostructured SiO_2nanopowderswere measured by using X-ray diffraction spectroscopy (XRD), field emission-scanning electron microscopy (FE-SEM), energydispersive X-ray spectroscopy (EDAX), high resolution-transmission electron microscopy (HR-TEM), surface area electron diffraction (SAED) patterns, andBrunauer-Emmett-Teller (BET)analysis.

2. Experimental

2.1 Materials

Chemicals and solvents of AR grade were purchased from Sigma Aldrich and Merckand were used without further purification.The sticky rice husk ash was collected fromSouth Korea.

2.2. Synthesis of silica nanoparticles

Nanostructured silica was synthesized fromrice husk ash through a simple acid pretreatment (chemical method). Sticky rice husk were burned in an open environment to collect their ash. 3.0 gof rice husk ash were first stirred with 45 mL of 10% HCl for 2 h to remove the metal ions inside. The metal ions were then removed from the rice husk ash,and these are denoted asleached rice husk ash (LRHA).The LRHA were filtered and washed with a large amount of deionized (DI) water and dried at 150°C for 24 h in an electric oven. The obtained dry powder weretransferred from a Petri dish to an alumina crucible and annealed at 700 °C with a ramp rate of 5°C min^{-1}in a muffle furnace at atmospheric pressurefor 2 h. Finally,we obtaineda white-coloredmesoporous silica (m-SiO_2)nanopowder.

2.3. Characterization of silica nanoparticle

A microstructural analysis of synthesized silica nanopowder were carried out fromX-ray diffraction spectroscopy (XRD), field emission-scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDAX), and transmission electron microscopy (TEM). The XRD (XRD, XPERT-PRO), patterns were obtained by using $CuK_{\alpha 1}$ as a radiation source (λ = 1.5405 Å) operating under a constant current of 30 mA at 40 kV with a diffraction angle (2θ) scan range of 5to 80°. The surface morphology and the chemical composition of the prepared SiO_2nanoparticles were examined by using FE-SEM (Hitachi, S-4800), EDAX (S-4800), and HR-TEM. The amorphous structure was further confirmed from the selected area electron diffraction (SAED) pattern.Adsorption-desorption isotherm tests were carried out for synthesizedsilica powder by using a Brunauer-Emmett-Teller (BET) (BELSORP-mini II, Japan) analyzer with the N_2 absorption technique at 77 K. The pore size distributions were derived from the adsorption branch of the isotherms by the Barrett-Joyner-Halenda (BJH) method.

3. Results and Discussion

Fig. 1shows the XRD pattern of mesoporous silica nanopowder synthesized from sticky RHA.The absence of sharp peak in the XRD pattern of mesoporous silica nanoparticle indicated the amorphous nature of the material.The prepared nanoparticle exhibited a broad intense peak at 2θ = 22°, which indicated the presence of silica nanoparticles. No other impurities were detected. Therefore, this economically-synthesized material is useful for various applications[2].

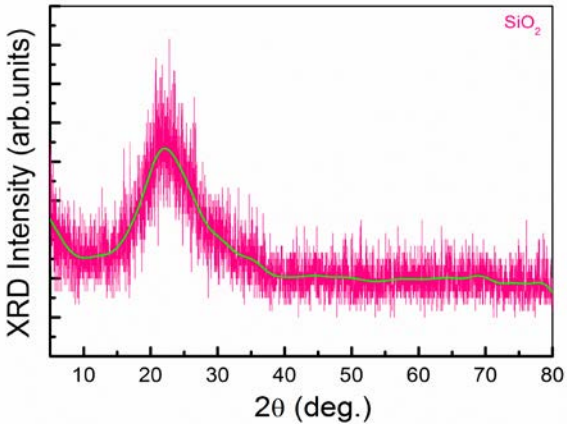

Fig. 1 XRD pattern of the synthesized porous SiO_2 nanopowder

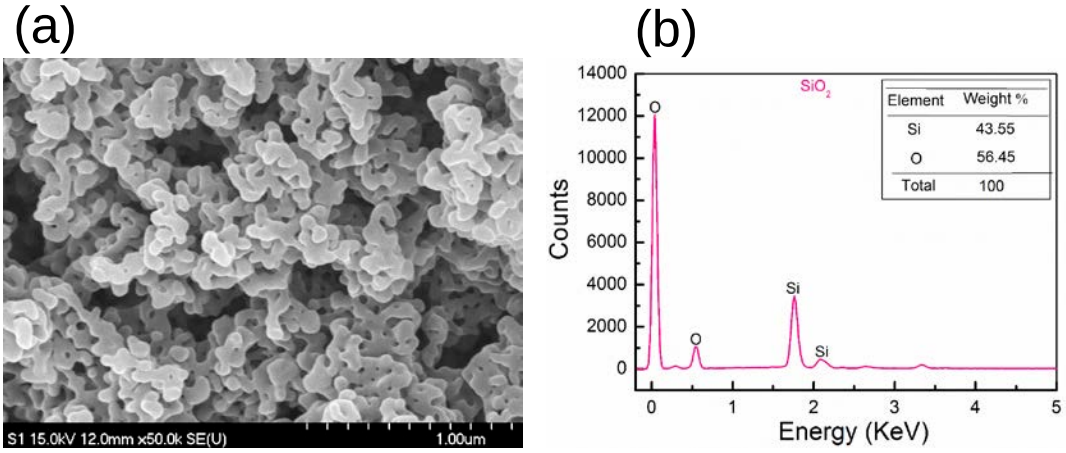

Fig. 2 FE-SEM image of synthesized mesoporous silicananoparticle.

Fig.2(a)shows FE-SEM image of the mesoporous silicananopowder synthesized from sticky RHA. The morphology of SiO_2consisted of cluster-type spherical nanoparticles.The SiO_2nanoparticles were obtained had a uniform surface morphology with respect to the uniform particle size distribution.Fig. 2(b) shows the EDAX spectrumof SiO_2 nanopowder. The elemental composition of Si and O determined from EDAX spectrum.The elemental compositions of Si and O wereobserved at a ratio ofSi:O = 43.55:56.45in terms of weight percentage (wt. %).

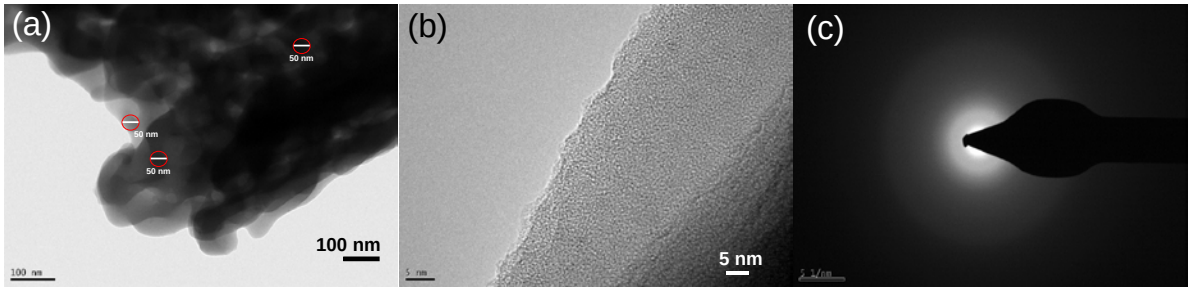

Fig. 3 TEM analysis of the SiO_2 nanoparticles: (a) bright field image,(b) HR-TEM image, and (c) SAED pattern.

The particle size distribution and the structure ofmesoporous silica nanoparticles were determined byusing HR-TEM and SAED-pattern. Figs. 3 (a), (b), and (c) show the bright field image, high resolution TEM, and SAED pattern of the mesoporous silica nanopowder, respectively.A bright-field TEM imageof the SiO_2 nanoparticles revealed the clusters of primary particles with an irregular geometry and a spherical shape along with a wide size distribution. The average diameter of the SiO_2 nanoparticles was observed to be 50 nm, and every primary particlewasinterconnected and adheredwith each other.The absence of uniform and periodic lattice spacing in the HR-TEM image also confirmed the amorphous nature of the mesoporous silica nanoparticles.The electron diffraction rings of the SAED pattern of the synthesized mesoporous silica nanopowdersindicated the amorphous phase of the main phase of silica nanopowder.From the microstructure and structural analysis of synthesized mesoporous silicananoparticle confirmed the uniform and amorphous state of the powder.

The surface area and the pore characteristics of the mesoporous silica nanopowder were determined by using the BrunauerEmmettTeller (BET) and BarretJoynerHalenda (BJH) methods Figs. 4(a), and(b) show the adsorption-desorption isotherm of the mesoporous silica nanopowder and pore diameter, respectively. The specific surface area of the mesoporous silica nanopowder was observed to be 7.1548 m^2g^{-1}. During nitrogen adsorption-desorption, the hysteresis loop generally appeared between the adsorption and desorption branches, which indicates the capillary condensation of porous structure. The characteristics of the SiO_2 nanopowder were detected from the non-hysteresis loop of the III-type model. It is indicated that the SiO_2 nanopowder was the porous material.

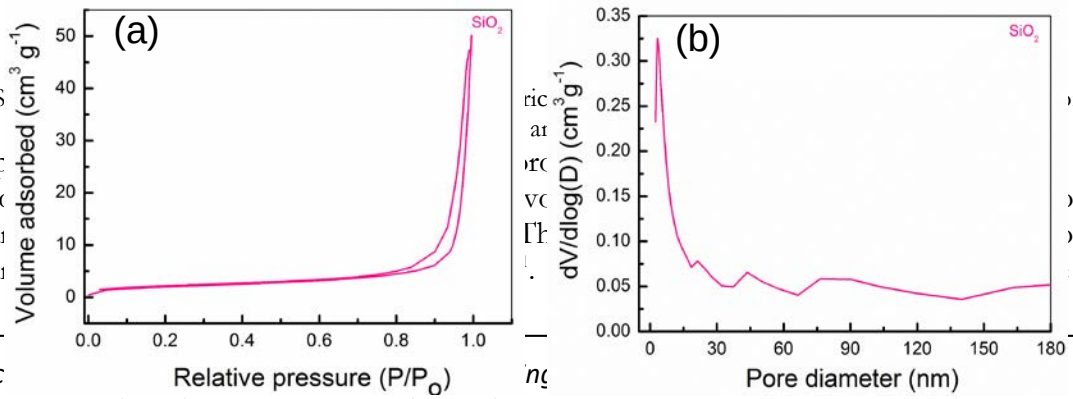

Fig. 4S ric f silica

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surface area becauseit was the least porous material. The pore volume of the mesoporous silica, nanopowderwas observed to be 0.0650 $cm^3 g^{-1}$and the average pore diameter is 36.34nm. Thus the results indicated the synthesized silica nanoparticles showed porosity and wider pore distribution.

4. Conclusion

MesoporousSiO_2nanopowderwassuccessfully synthesized from sticky RHA through a simple acid pretreatment method.The microstructural and elemental composition analysisconfirmed the spherical shape and purity of the SiO_2 nanoparticles. The SEM and TEM analyses of the silica nanopowder revealed that SiO_2had the particle size 50 nm and the surface area 7.1548 m^2g^{-1}. The absence of sharp peaks in the XRD pattern and the electron diffraction rings in the SAED pattern confirmed the amorphous nature of the material. The biogenerated SiO_2nanoparticles synthesized from sticky rich husk ash are considered to be the most compatible material for energy storage and optoelectronic applications.

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