

Production and Characterization of Amorphous Silica Nanoparticles from Coconut Shell and Coir

Jeleel Adekunle Adebisi¹, Jeebanjyoti Muduli², Amal Rherari³, Ismaila I. Ahmed¹, Mubarak Opeyemi Bello^a, Muthiah Haris^b

^aDepartment of Materials and Metallurgical Engineering, University of Ilorin, Nigeria

^bDepartment of Physics, Karunya University, Karunya Nagar, Coimbatore 641 114, India

^cDepartment of Physics, Laboratory of Optoelectronic and Physical Chemistry of Materials, Ibn Tofail University, Morocco

*Corresponding author: bello.mubarak007@gmail.com

Abstract

Keywords:

coconut coir; coconut shell; agricultural wastes; silica; sol-gel.

The exponential growth of the wireless data traffic and Amorphous silica nanoparticles were successfully synthesized from an abundant agricultural waste, coconut coir and shell, via an eco-friendly calcination and sol-gel process. The raw ashes were calcined at 700 °C and treated with hydrochloric acid to remove soluble metallic impurities. Subsequent alkaline extraction and acid precipitation yielded silica gel, which was dried to obtain the final product. Comprehensive characterization using SEM, EDX, XRD, and FT-IR confirmed the formation of amorphous silica nanoparticles with sizes below 100 nm. EDX analysis indicated high silica content, with residual impurities such as aluminum and potassium identified. The particles exhibited a strong tendency to agglomerate due to inter-particle hydrogen bonding. This work demonstrates a simple, cost-effective route to valorize coconut waste into valuable nanoscale silica, presenting a promising precursor material for applications such as silicon nanoparticle production, composites, and adsorbents.

1. Introduction

Agricultural wastes have been utilized for the production of several useful materials in order to reduce their disposal challenges. Most often, these wastes are generated and disposed indiscriminately or burnt, which results in environmental pollution with adverse effects on the climate (IEA, 2016). The side effects on climate have been major challenges across the globe because they lead to the death of about 160,000 people annually (Grebmeier et al., 2011; McNutt et al., 2015). India utilizes approximately 78% of its landmass, about 2,564,065 square kilometers, for the production of various agricultural products and ranks third in the production of eggs, oranges, coconuts, tomatoes, peas, and beans (FAO, 2011). Literature has shown that agricultural wastes have been used as solid fuel briquettes, adsorbents, cellulose, activated carbon, silica, silicon, refractory and ceramic products, livestock feed, inhibitors, biofuels, construction materials, lignin, and composite reinforcement (Achinivu et al., 2014; Adepoju et al., 2016; Bunmai et al., 2018; Heuzé et al., 2014; Ki et al., 2013; Le Normand et al., 2014; Liu et al., 2014; Odusote et al., 2016; Olajide et al., 2014). Silica has been used as an intensive blue light emitter, fining agent in the food industry, powder flow agent in the pharmaceutical industry, extra-terrestrial particles collectors, DNA and RNA extractors, hard abrasives in toothpaste, desiccant, capacitors, and silicon production (Chattoraj et al., 2011;

Mohammad-Rezaei & Razmi, 2016; Negre et al., 2016; Tan and Yiap, 2009; Westphal et al., 2014; Yu et al., 1998; Zemnukhova et al., 2012).

Silica occurs naturally as quartz with the largest percentage in the earth crust. It is crystalline in nature with low reactivity. Amorphous silica on the other hand find applications in many areas owing to its advantage of being highly reactive. The non-crystalline type has been synthesized from sodium silicate (Sudirmana et al., 2012), water glass (Lee et al., 2007), and tetraethoxysilane (TEOS) (Shimura and Ogawa, 2007). It has also been produced from agricultural wastes using several methods as reported in reviews (Adepoju et al., 2016; Espíndola-Gonzalez et al., 2010; Zemnukhova et al., 2012). It is usually prepared by reacting sodium carbonate powder and quartz sand at high temperature to form sodium silicate, which will then react with sulphuric acid to precipitate silica (Soltani et al., 2015). The methods used for synthesis from agricultural wastes involve a combination of processes like acid treatment, partial burning (charring), burning, calcination, leaching, enzymatic treatment, pyrolysis, hydrolysis and sol-gel (Mansha et al., 2011; Nayak & Bera, 2012).

Among wastes generated in India, coconut wastes stand out as they litter farmlands, residential and industrial areas because coconut flesh/juice's economic and social importance. Coconut is a fruit of an Arecaceae plant (palm family) and can be found everywhere across India. The fruit is 55% coir, 15% shell, and 30% flesh (meat) and juice (Bello et al., 2016). The coir (fibrous part) is useful for mats, ropes, sacks, door mats, brushes, boat caulks, compost, and fiber for mattresses (Grimwood and Ashman, 1975). Both coir and shell are used as fuels with/without carbon enrichment. With all these utilizations, several coir and shells are domestically disposed indiscriminately. The ash obtained from both contains a huge amount of silica, which can be extracted using simple methods (Sivasubramanian and Sravanthi, 2015). In this present work, coconut shell and coir have been used to synthesize amorphous silica using calcination and the sol-gel approach.

2. Materials and Methods

2.1 Materials

Coconut shells and husks were collected at Karunya University farm settlement, Karunya Nagar, Coimbatore, India. Sodium hydroxide and hydrochloric acid used are analytical grades (purchased at NICE Chemicals Ltd., Kerala, India). Filtration was carried out using filter paper (Whatman No 41) on a vacuum filter.

2.2 Methods

The procedure used in this work is as highlighted in Fig. 1. This procedure involves separation of the coir and shell from the main fruit, then removal of moisture, volatile matter and carbon to get ash. This is followed by acid treatment to remove soluble oxides of some metals. The sol-gel involves the formation of silicate solution (solation) from ash (see Equation 1) and the neutralization of the alkaline solution (gelation) to precipitate silica gel (see Equation 2) dispersed in a sodium chloride solution. Centrifuging was carried out to separate the silica from the NaCl solution with washing and rinsing with double-distilled water (DDW) to remove NaCl.

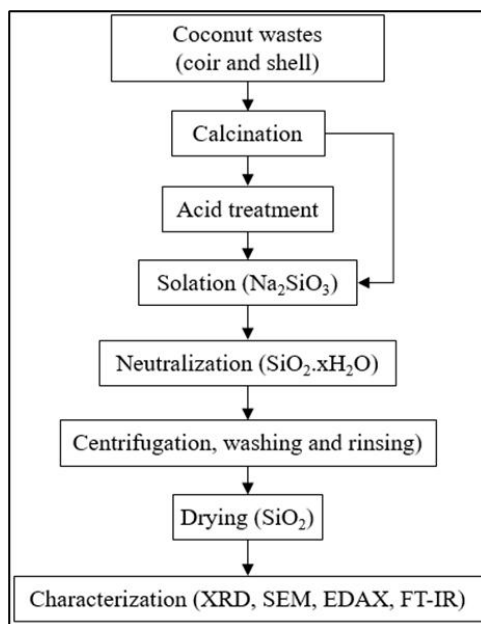
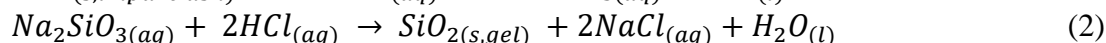
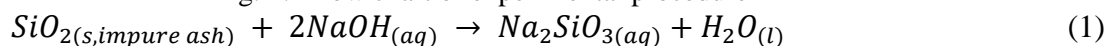


Fig. 1: Flow chart of experimental procedure



2.2.1 Preparation of Coconut Coir and Shell Ashes

15 pieces of coconut fruits were selected and manually separated into coir, shell and meat. The coir and shells were sun-dried for 14 days before calcination in a muffle furnace. The samples were put in the furnace and then heated at 6 oC/min to 700 oC. The temperature was held for 3 hours and then off with samples left to cool for 12 hours. The samples were thereafter removed and labelled as coconut coir ash (CCA) and coconut shell ash (CSA) for coir and shell, respectively.

2.2.2 Acid Treatment of Coconut Coir and Shell Ashes

A total of 23 g of CCA and CSA were leached using 1.0 M HCl and stirred at 600 rpm for 60 minutes. The resulting residues were collected by filtration, rinsed with DDW, and dried in an oven at 105 °C for 24 hours. The dried samples were labelled TCCA and TCSA for CCA and CSA, respectively.

2.2.3 Production of silica

For the preparation of sodium silicate from CCA, CSA, TCCA, and TCSA, 12 g of each sample were added to NaOH and heated at 90 °C for 60 minutes. 3.0 and 1.0 M of NaOH were used for TCCA and TCSA, while 3.0 M was used for CCA and CSA. The mixture was allowed to cool and then filtered using Whatmann No 1 filter paper. The filtrate was titrated with 1.0 M HCl until the pH of 6.0 to ensure neutralization of the initial NaOH. This was left to age for 18 hours to get a clear supernatant and NaCl solution. The supernatant was decanted and the remaining silica gel solution was centrifuged at 4000 rpm for 10 mins. The supernatant was decanted and DDW was added for rinsing. This step was repeated until there were no traces of acid using the pH meter. The silica gel obtained was then dried in the oven at 65 oC for 24 hours. The silica obtained was then pulverized using agate mortar and stored for characterization.

2.2.4 Characterization

Silica produced from CCA, CSA, TCCAs and TCSAs were characterized with SEM, EDX, XRD and FT-IR. SEM was carried out to investigate the morphology and sizes of the silica. EDX was carried out to investigate the chemical composition and invariably the purity of the silica. XRD was used to determine the structure of the prepared silica, while FT-IR investigated the functional groups present.

3.Results and Discussion

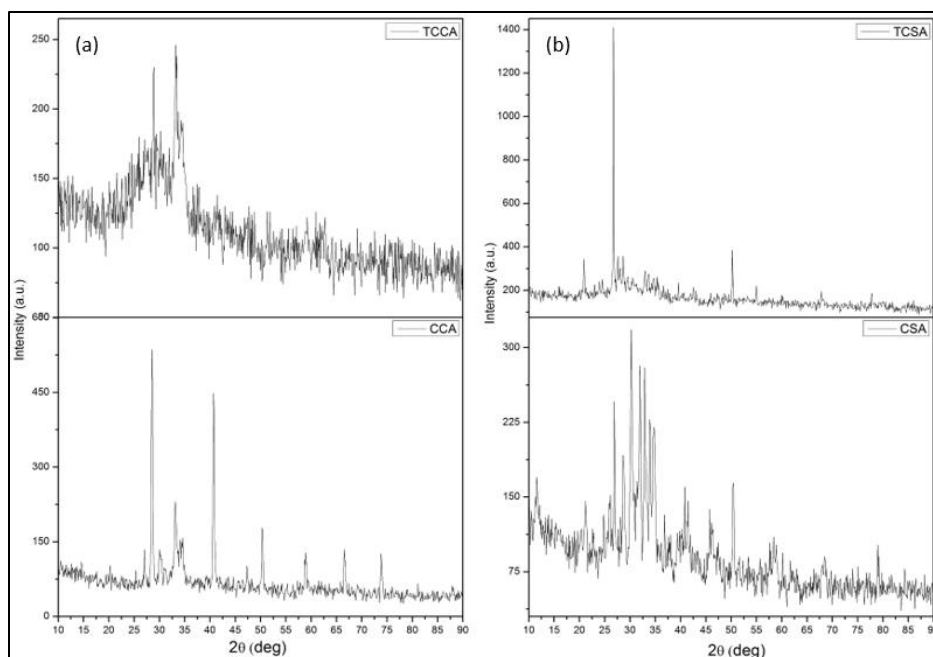


Fig. 2: Effect of acid treatment on CCA and CSA

The amorphous nature of silica produced from both the coir and shell, with/without treatments are shown in Fig. 3. The crystalline peaks from Fig. 3 (a) and Fig. 3 (b) are unwashed NaCl from the solution. The peaks are found to correspond to JCPDS card numbers: 78-0751 and 01-0994. The sodium chloride shown in Equation (2) is formed due to the neutralization of the NaOH reagent used during the alkaline treatment by HCl. This phase can be removed using hot water washing and rinsing which has been reported to be effective for removal of any traces of NaCl (Yuvakkumar et al., 2014).

Table 1 shows the chemical compositions of silica obtained through the various approaches. The major impurity in the silica obtained is aluminium (as Al_2O_3), which is an amphoteric oxide. This forms precipitates when leached with acid and soluble hydroxide when treated with base. The use of a weak base for the solution of CCA yields silica free of aluminium, while it seems difficult for CSA. Hence, removal of this oxide is a concern. The Na and Cl present can be removed by hot water washing or repeated washing of the silica gel until free of the salt. Fig. 4 shows that all the silica produced is below 100 nm. This is as a result of the method used, which is categorized as an appropriate approach to the synthesis of nanoparticles categorized as bottom-up approach in the review of Adebisi et al. (2017). The micrographs also show that there is agglomeration in the procedure used.

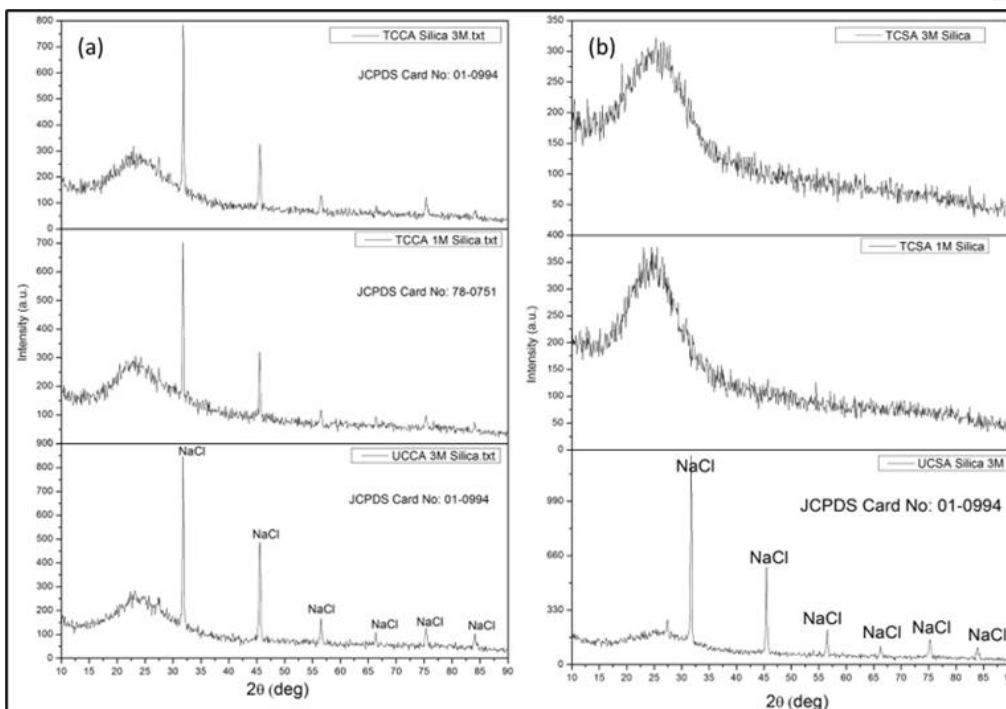


Fig. 3: Silica produced from CCA, TCCA, CSA, and TCSA

Table 1: Chemical composition of silica produced

Elements	Composition of silica (wt. %)					
	UCCA 3M	TCCA 1M	TCCA 3M	UCSA 3M	TCSA 1M	TCSA 3M
O	54.04	45.3	57.14	56.34	64.49	54.33
Na	4.31	8.76	3.37	4.13		
Al	2.82		2.51	6.12	19.78	5.11
Si	31.33	32.57	32.43	24.62	15.73	40.56
Cl	5.57	11.7	3.46	3.61		
K	1.93	1.67	1.09	5.19		

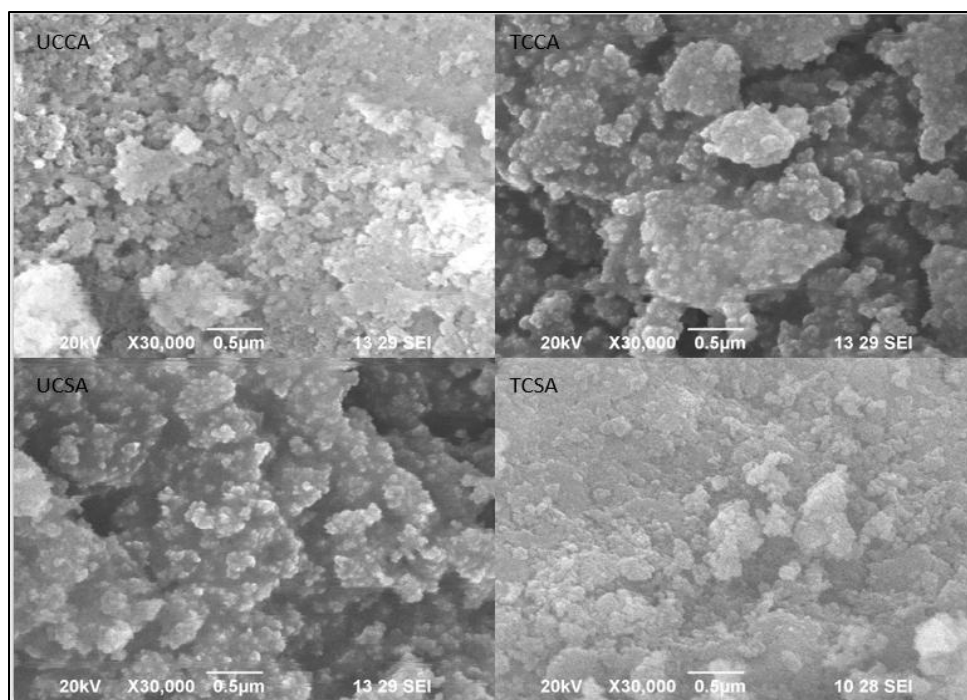


Fig. 4: SEM micrographs for untreated and treated coconut coir and shell silica

The FT-IR spectrum of silica produced from the coir and shell are shown in Fig. 5. Silica is characterized by a band between 400 and 1300 cm^{-1} (Carmona et al., 2013). The spectra from prepared silica exhibit bands at 448, 796 and 1085 cm^{-1} , corresponding to characteristic rocking of the Si-O bond, its bending and symmetric and asymmetric stretching of the Si-O-Si bond, respectively (Espíndola-Gonzalez et al., 2010). Drying the samples at 65 $^{\circ}\text{C}$ left the samples with OH and H-O-H bonds for silanol and adsorbed water (Carmona et al., 2013). The band at 1642 cm^{-1} corresponds to H-O-H twisting, while bands spreading from 2600 to 3800 cm^{-1} represent stretching vibrations of the surface silanols (Si-OH) groups excited by hydrogen bonds of either water adsorbed or those between Si-O molecules (Carmona et al., 2013; Rafiee et al., 2012). The high transmittance values of silica obtained from the untreated samples (CCA and CSA) translate to low absorbance compared to those from treated samples. This characteristic high peak of the untreated samples has been reported by Carmona et al. (2013).

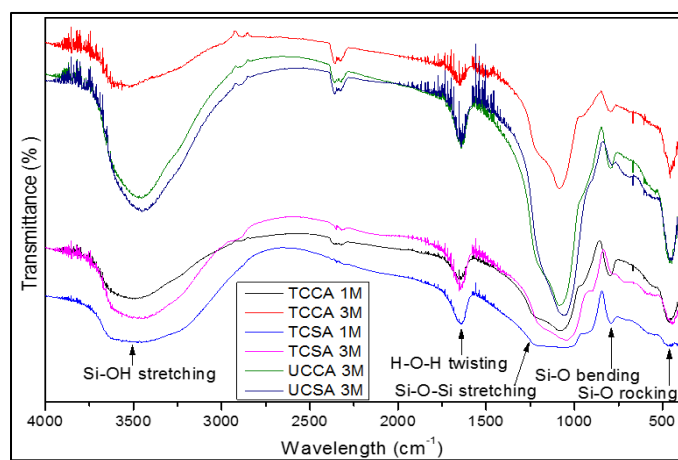


Fig. 5: Infrared bands of prepared silica

4. Conclusion

This study successfully demonstrated the valorization of coconut coir and shell into amorphous silica nanoparticles using a straightforward integrated process of calcination, acid leaching, and sol-gel synthesis. Characterization results confirmed the amorphous nature, nanoscale size (<100 nm), and high silica purity of the produced materials, although EDX revealed the presence of residual Al and K impurities, alongside Na and Cl from the synthesis reagents. A key morphological observation was the high degree of particle agglomeration, attributed to strong interfacial interactions between surface silanol (Si-OH) groups. Despite this, the method presents a sustainable and economically attractive pathway for producing nanosilica. The produced silica holds substantial potential for use as a low-cost feedstock in the synthesis of silicon nanoparticles and for various applications in nanocomposites, catalysis, and adsorption technologies.

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