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PRODUCTION OF SILICON NANOPARTICLES FROM SELECTED AGROWASTES FOR SOLAR APPLICATIONS

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ABSTRACT

Electricity generation and distribution in Nigeria is currently grossly inadequate. However, the solar energy potential of Nigeria encourages investment in photovoltaics (PV) technology of which silicon is an initial material. Some agricultural wastes have been utilized for silicon production through a simple method. The aim of this research is to develop an alternative utilization for some agricultural wastes as potential sources of silicon that could be deployed for PV cells. In this study, cassava periderm, maize stalk and cob were utilized as novel sources of silicon nanoparticles. Silica nanoparticles were produced using modified sol-gel method and was thereafter reduced using magnesium to synthesize silicon nanoparticles. The products were characterized using X-ray diffractometer, Energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, Raman and transmission electron microscopy. The results showed that silicon nanoparticles with particle sizes less than and purity of 33.98 nm and 98.89 %, 31.20 nm and 99.89 % and 32.88 nm and 99.95 % for cassava periderm, maize stalk and maize cob, respectively were successfully produced.

Keywords: *Agricultural Wastes, Silicon Nanoparticles, Amorphous Silica, Sol-Gel, Metallothermic Reduction*

INTRODUCTION

Energy is very crucial to the sustainability of the modern society without which life will be miserable in this modern world. Electricity is a green source of energy since it can easily be transformed to other forms of energy with little or no pollution. Nigeria electricity generation and consumption fall short of demands leaving the populace in darkness and resulting in low productivity. Nigerians depend mostly on fossil fuel utilization for their basic energy needs due to unavailability of clean energy. Petroleum products and biomass are the reliable option for citizens by which they improvise their energy needs coupled with use of combustion engines for domestic and industrial electricity generation. Utilization of biomass such as charcoal encourages deforestation which is also a bane of our ecosystem (Chidumayo and Gumbo, 2013). Combustion of fossil fuels generates greenhouse gases and chlorofluorocarbons (CFCs) as either primary or secondary products of combustion which often result in climate change (Moore III *et al.*, 1999). Side effects of climate change has been reported to be associated with death of about 160,000 people annually (Asif and Muneer, 2007).

According to Energy Commission of Nigeria (ECN), power generation requirement is put at 31,210 MW against the 4,389 MW available (Salau, 2015). This vogue energy consumption per capita of Nigeria is meagre when compared with those of Algeria, Egypt and South Africa (Adebisi *et al.*, 2017). Energy mix was suggested as a means of improving the energy profile in Nigeria as proposed by Akin (2008). Adurodija *et al.* (1998) investigated the solar photovoltaics (PV) potential in Nigeria to provide electricity in isolated communities not connected to the national grids. Nigeria has the potential to generate about 600,000 MW of electricity by deploying solar PV panels of only 5% efficiency from just 1% of her land mass (NASENI, 2014; Oji *et al.*, 2012).

Silicon is the leading commercialized PV materials due to its relatively high efficiency. Its initial high cost of production prompted researchers and industries to investigate into thin film technologies for materials reduction and improvement of the cell performance (Veneri *et al.*, 2010; Gorter and Reinders, 2012; Mercaldo *et al.*, 2013). Silicon nanoparticles are usually produced from bulk silicon feedstock using laser ablation, milling or attrition. Furthermore, they are also synthesized via various chemical routes such as electron beam evaporation, laser-assisted electrochemical etching, plasma-enhanced chemical vapour deposition, pulsed laser deposition and combustion synthesis (Xie *et al.*, 2003; Iacopi *et al.*, 2007; Maiti *et al.*, 2008; Li *et al.*, 2009; Eisenhawer *et al.*, 2011; Larbi *et al.*, 2011; Won *et al.*, 2011). However, production from bulk materials requires silicon ingot from either chemical or metallurgical processes which are either energy intensive, generates toxic substances or slow and generally complicated (Braga *et al.*, 2008). These prompted researchers to investigate other routes for production of silicon nanoparticles (Venkateswaran *et al.*, 2013). Agricultural wastes have thus been employed for this purpose to mitigate their adverse environmental impacts. Hence, rice husk, rice straw, horsetail, larch needles and bamboo leaves have been reported for this synthesis (Zemnukhova *et al.*, 2012; Venkateswaran *et al.*, 2013; Aminullah *et al.*, 2015).

The silicon production methods so far employed include production of silica via various routes and its reduction by either metallothermic or carbothermic reduction (Hunt *et al.*, 1984; Mishra *et al.*, 1985; Barati *et al.*, 2012). This method is cost effective and has been reported to possess future prospects (Laine, 2012; Laine *et al.*, 2013; Laine and Marchal, 2015). The aim of this present work is to investigate production of silicon nanoparticles from some agricultural wastes that are of less economic importance in Nigeria. Nigeria is the largest producer of cassava generating more than 3.4 million tonnes of cassava peelings as at 2009 (Heuzé *et al.*, 2014). This constitute about 5 – 15 % peelings from typical tubers (Nwokoro *et al.*, 2005; Aro *et al.*, 2010). Cassava periderm is the part of cassava peelings that is not consumed by any livestock. Nigeria also produces maize that generates stalks and cobs that are of less economic importance (CIA, 2015). Hence, the imperative to find useful utilization of these wastes to reduce the challenges associated with their disposal.

MATERIALS AND METHODS

Materials

The cassava periderm (CP) was extracted from cassava that was purchased from Betterlife market, Isale-Osun, Osogbo, Osun State, Nigeria. Maize stalk (MS) was harvested from the University of Ilorin farm settlement, Ilorin, Kwara State, Nigeria. Maize cob (MC) was commercially in Osogbo, Osun State, Nigeria. Analytical grade magnesium powder (LOBA Chemie, 99 % purity) was purchased from Modern Scientific Company, Coimbatore, India. Other reagents used were purchased from Precision Scientific Co., Coimbatore, India. They include; sodium hydroxide pellets (RANKEM, 98.30 % purity), hydrochloric acid (NICE, 99.896 % purity), acetic acid (NICE), polyvinyl alcohol solution (PVA) (LOBA Chemie) and ethylene glycol (NICE). Double distilled water (DDW) was used for rinsing throughout the experimental procedure.

Methods

The agricultural wastes were prepared as described in Adebisi *et al.* (2019) while silica nanoparticles were produced as described by Adebisi *et al.* (2018). Each silica nanoparticles and magnesium powder were ground and mixed homogeneously (in mass ratio of 1:1) with 25 % excess magnesium to accommodate surface MgO. Pellets were produced using 4 % PVA solution as binder after pelletization at 10 MPa. The pellets were reduced at 650 ^{o}C for 30 min in a muffle furnace to obtain silicon and magnesium oxide as shown Eq. 1. The reduction product was thereafter leached and rinsed in seven stages (to remove MgO and other impurities) as shown in Table 1 and dried at 80 ^{o}C for 24 hours. The silicon produced was characterized using energy dispersive X-ray spectroscopy (EDS), X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman and transmission electron microscopy (TEM).

$$SiO_{2(s)} + 2Mg_{(s)} \rightarrow Si_{(s)} + 2MgO_{(s)} \qquad \text{(Eq. 1)}$$

Table 1: Leaching reagents concentrations and post-reduction purification parameters

Leaching Steps	**leachates and rinsing parameters**
1	50 % acetic acid at room temperature for 15 min
2	50 % acetic acid at room temperature for 10 min
3	33 % hydrochloric acid at room temperature for 10 min
4	33 % hydrochloric acid at room temperature for 15 min
5	Boiled and leached in 50 % hydrochloric acid for 15 min
6	Boiled and leached in HCl:HNO_3:DDW at 1:1:2 for 15 min
7	Rinsed 8 times with DDW to get rid of any traces of acids

RESULTS AND DISCUSSION

Chemical Analysis of Silicon Nanoparticles

The EDS spectra in Fig. 1 show silicon peaks to be very high in most of the samples produced. Few low intensity peaks of impurity elements of O and Mg are observed except in maize cob where the peak of O is arbitrarily high. This small amount of oxygen may be due to surface silicon oxidized when in contact with air (Raider *et al.*, 1975; CARIM *et al.*, 1987; Petrova *et al.*, 2000; Henrion *et al.*, 2002). Oxidation of silicon to silicon (mono)oxide is a feasible reaction even at ambient conditions. The abnormal high oxygen in MC silicon may be attributed to the presence of unreduced silica. The silicon nanoparticles produced contain 93.69, 90.63 and 59.10 % for CP, MS and MC, respectively. Though, CP silica nanoparticle used for reduction contains lower silicon but with highest elemental impurities up to 15.23 % that might also take part in reduction of silicon oxide.

Structural Properties of Silicon Nanoparticles

XRD patterns of reduction products are presented in Fig. 2. All the reduction products contain mainly silicon (JCPDS code 27-1402), magnesium silicide

(JCPDS code 35-0773) and magnesium oxide (JCPDS code 87-0653), all of cubic crystal structure. MgO is the prominent phase in the samples with associated peaks at 37.04, 43.02, 62.42, 74.78 and 78.73°. The silicon peaks were observed to occur at 28.60, 47.51, 56.40 and 88.40°. Traces of magnesium silicide was observed in the reduced sample. This might be due to reaction of the excess magnesium with the desired silicon nanoparticles. The formation of Mg_2Si during the metallothermic reduction has been reported for silica produced from different sources (Larbi *et al.*, 2012; Al Mubarok *et al.*, 2014). The XRD pattern for Mg utilized for the reduction is also presented as commercial Mg. Its associated peaks are not observed in the reduction products but for the reaction products are similar to those reported by Larbi *et al.* (2012).

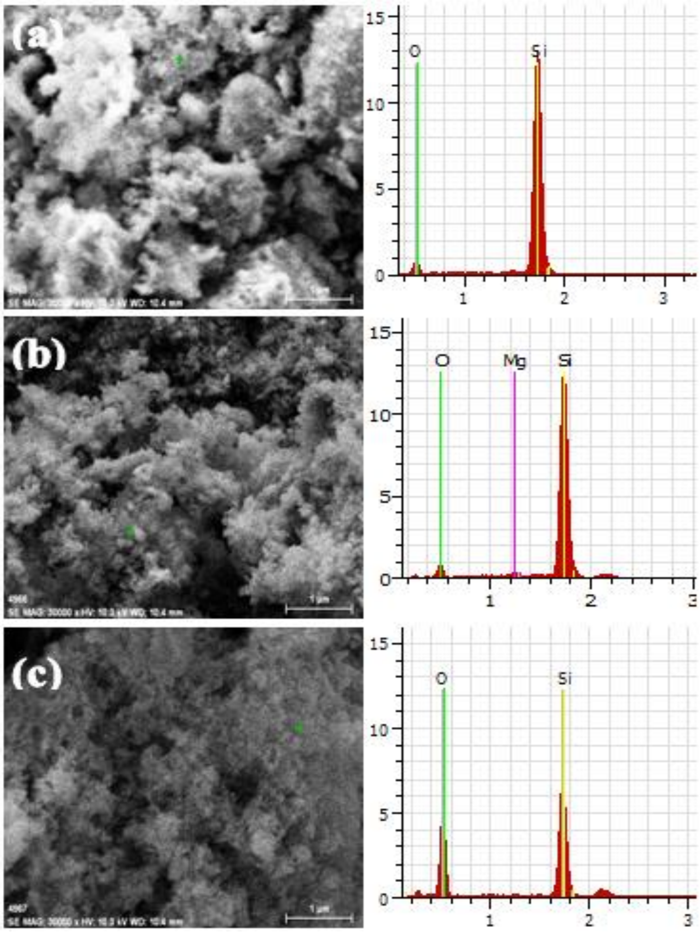

Fig. 1: SEM micrographs and EDS spectra for silicon nanoparticles prepared from (a) CP, (b) MS and (c) MC

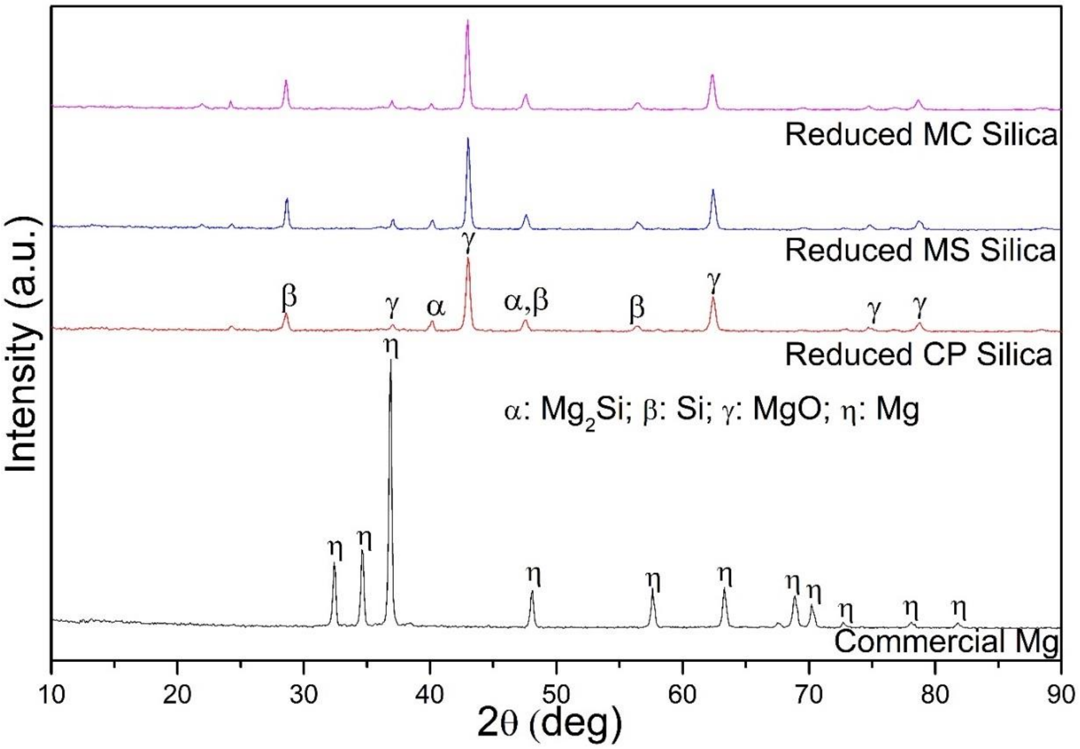

Fig. 2: XRD patterns for Mg and reduced silica prepared from agricultural wastes

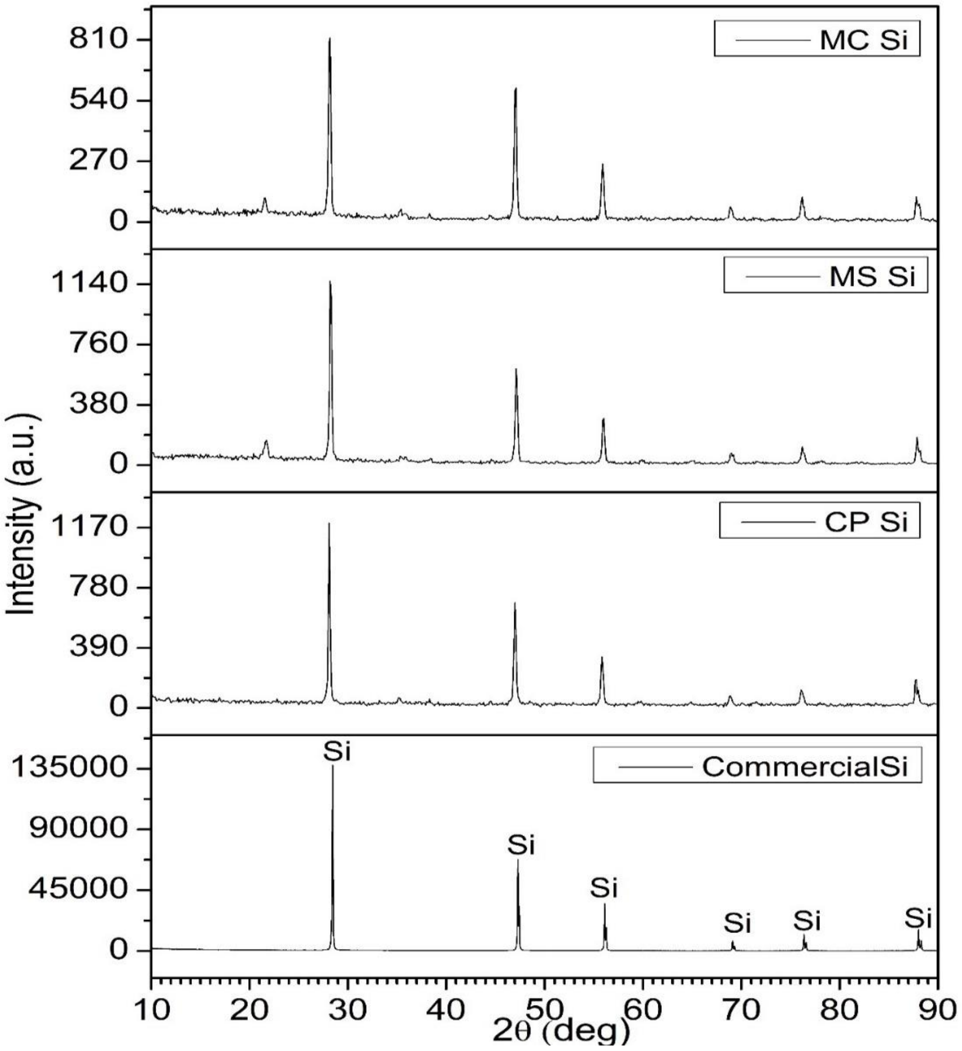

Fig. 3: XRD patterns for commercial and produced silicon particles

The solubility of MgO and Mg_2Si in organic acids have been reported (Larbi *et al.*, 2012). The XRD patterns for commercial silicon powder and silicon prepared after leaching procedure described in

Table 1 are presented in Fig. 3. They were identified as cubic silicon with JCPDS code 27-1402. The peak list of CP silicon conforms with the commercial silicon in terms of diffraction angles and relative percentage intensities. The XRD patterns of maize wastes (MS and MC) showed a distinct peak at position 2θ of 21.80°. This might be due to the presence of unreduced silica since the peak conforms with the highest peak of annealed silica earlier reported (Adebisi *et al.*, 2018). These results compared well with the results of silicon prepared from different sources (Larbi *et al.*, 2012; Zemnukhova *et al.*, 2012; Venkateswaran *et al.*, 2013; Arunmetha *et al.*, 2018).

Purity Analysis of Silicon Nanoparticles

The FT-IR of silicon nanoparticles produced are presented in

Fig. 4. The silicon nanoparticles show existence of Si-O band at 457.15 cm^{-1}. The bands at 797 and 882 cm^{-1} are associated with Si-Si and Si-H, respectively. These three bands have been reported in literature for typical silicon functional groups (Zemnukhova *et al.*, 2012; Venkateswaran *et al.*, 2013; Arunmetha *et al.*, 2018). Silicon terminated by O and H has been extensively investigated by Mawhinney *et al.* (1997). Similarly, the presence of Si-O-Si band at 1086 cm^{-1} which is attributed to oxidation and wet etching of silicon in aqueous media. All other bands are those featured with silica as discussed in Adebisi *et al.* (2018). It is pertinent to note that Si-O-Si band at 1086 cm^{-1} is more pronounced in MS and MC silicon nanoparticles. This may be the peak anonymous with maize silicon powders presented in Fig. 3.

Raman shifts for silicon reported in literature vary slightly which might be due to characteristics band shift due to structural variations (Swatsitang and Krochai, 2009; Park and Choi, 2014). Park and Choi (2014) and Swatsitang and Krochai (2009) reported 516 and 519.9 cm^{-1} for silicon produced, respectively. Tuschel (2017) work shed more light on the reason Raman spectra of crystalline and amorphous solids differ while 520 cm^{-1} was reported for single crystal silicon. As shown in Fig. 5, Raman shifts exist at 513, 511 and 514 cm^{-1} for MC, MS and CP silicon nanoparticles, respectively. These values are in close proximity with those reported which confirm production of silicon in this investigation.

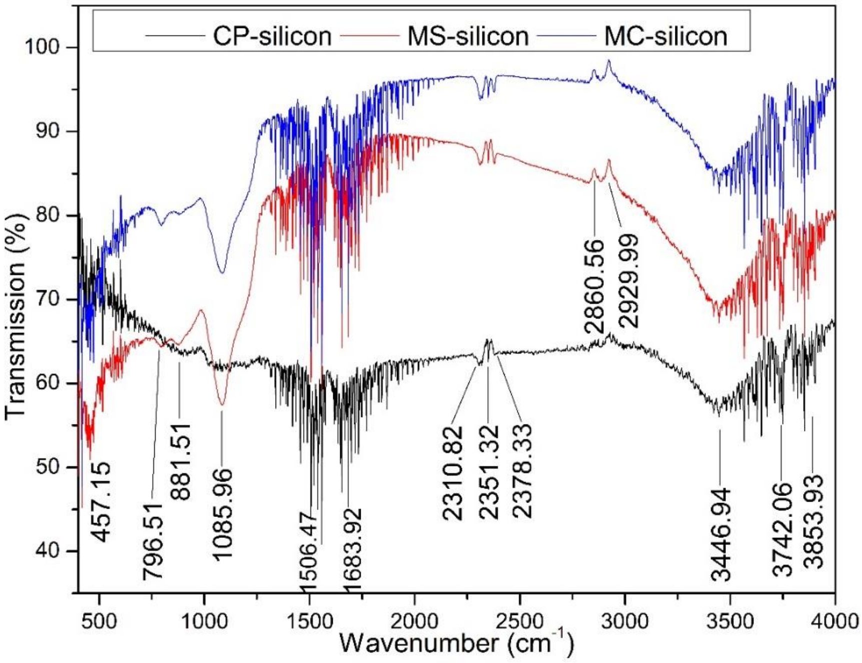

Fig. 4: FT-IR spectra for silicon nanoparticles prepared from CP, MS and MC

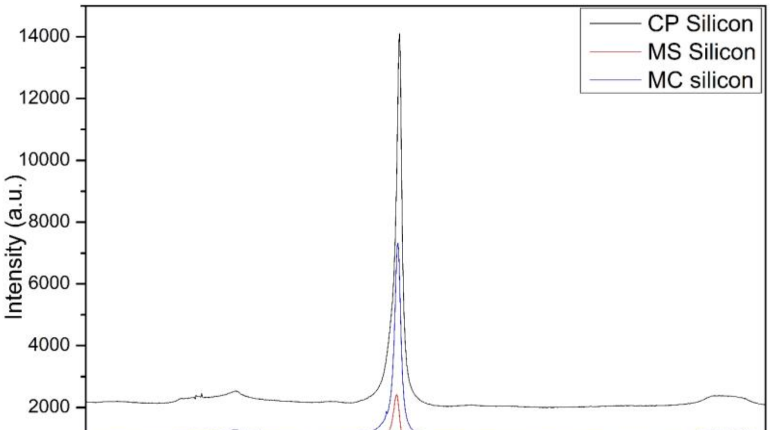

Fig. 5: Raman spectra for prepared silicon nanoparticles

Size Determination of Silicon Nanoparticles

Fig. 6 shows the TEM images of silicon nanoparticles produced. The particle sizes range from 7.85 – 33.98, 14.85 – 31.20 and 17.20 – 32.88 nm for CP, MS and MC, respectively. The presence of agglomerated silicon nanoparticles was observed in maize wastes unlike fine and short-range particle distribution in CP silicon nanoparticles.

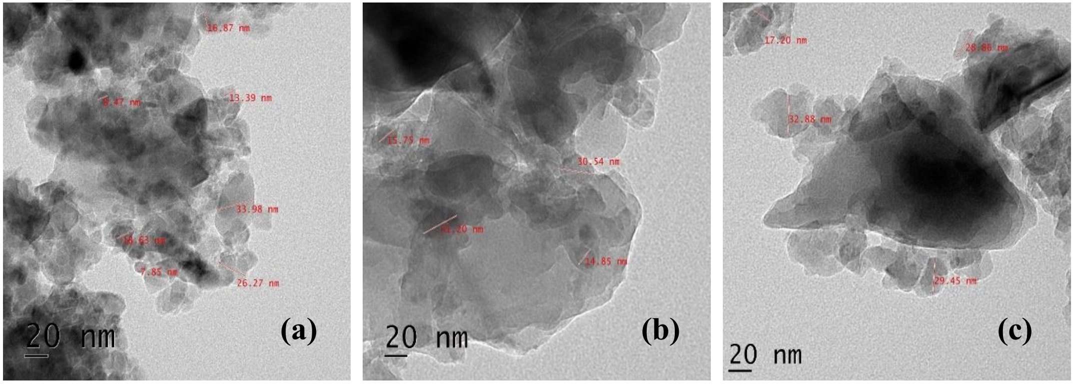

Fig. 6: TEM images for silicon nanoparticles prepared from (a) CP, (b) MS and (c) MC

CONCLUSION

The selected agricultural wastes have been successfully utilized for synthesis of silicon nanoparticles using a combination of modified sol-gel method and metallothermic reduction. The silicon produced could be dispersed in solvent and sprayed on appropriate substrate in semiconductor/photovoltaic application. This novel approach to have established more agricultural wastes that could be employed for synthesis of a relatively cheap silicon nanoparticles.

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