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Green Synthesis of Silicon Carbide from Sugarcane Bagasse through Magnesiothermic Reduction: A Potential Biomaterial for Photovoltaic Solar Cell

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Abstract

Sugarcane bagasse is the most abundant agricultural waste in terms of tonnage in the Philippines. This biomass can be converted into silicon carbide (SiC) – an important material for photovoltaic (PV) cells. SiC was prepared at 600 °C for 4 hours with the use of magnesium powder as a catalyst and it was further enhanced by doping through the solvothermal method. The successfully synthesized SiC appeared grayish in color having an average yield of 8.56%. The SiC was doped with varying amounts of urea (0.1, 1.0, 2.0, and 3.0, 0.02 M), an n-type dopant, and carried out in triplicate basis. Incorporation of n-type dopants increased its capability to be a good built-in voltage and absorbent of light. Effective band-gap energies of semiconductor material for the PV cells were in the range of 1.0-1.7 eV. Urea-doped SiC exhibited a higher wavelength compared with undoped SiC, which could imply their differences in band-gap. The conductance testing showed that electrical conductivity established a positive relationship with dopant concentrations. Appeared to be crystalline in nature, the surface morphology of doped and undoped SiC was determined through scanning electron microscope. The X-ray diffraction patterns confirmed the crystallinity of the synthesized material. The elemental analysis and vibrational frequencies through energy dispersive X-ray and Fourier transform infrared analyses proved the presence of silicon and carbon in the material. Therefore, sugarcane bagasse can be processed chemically to generate new products for solar cell applications employing simple and low-cost method.

***Keywords**:* urea-dopant, solvothermal synthesis, photovoltaic cell, sugarcane bagasse

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1. Introduction

Sugarcane bagasse is a fibrous material that remains after sugarcane stalks are crushed to extract their juice (Aloria *et al.*, 2017). It is the number one agricultural waste in terms of tonnage in the Philippines (Philippine Statistics Authority, 2018). Sugarcane bagasse in ash form is a unique energy source as it is globally available and renewable. For decades, the bagasse waste has been burned in the fields, thereby creating a large amount of pollution. However, the trends today are changing and environmental awareness is driving the prudent use of the bagasse (Swarnakar and Choubey, 2016).

Sugarcane bagasse and its ash are mainly composed of silica and carbon, which could be synthesized into silicon carbide (SiC). Silicon currently plays the most dominant functional role in commercial semiconductor applications owing to its high stability, non-toxicity, high carrier mobility and high fabrication process-ability (Luongo *et al.*, 2019). Thus, silicon has a significant impact on the modern world technologies and economy especially in the application of solar cells.

The SiC is a wide energy band-gap semiconductor that is used in photovoltaic (PV) cell production. The PV technology has an exciting prospect in fulfilling the world’s energy needs in the future without relying much on sourcing from non-renewable resources (Chowdhury *et al.*, 2020). Hence, it could lessen the adverse effects on the environment as well as in the economy of tapping energy from non-renewable means. It is expected that producing clean energy through PV-based materials will become the global energy source in the near future (Xu *et al.*, 2018).

Magnesiothermic reduction (MR) has been widely used in producing silicon structures at a low temperature conditions. The conventional method, carbothermal reduction, requires a lot of energy and high reaction temperature around 2000 °C that could greatly affect the integrity of the sample. MR offers a facile yet efficient method while preserving the intricate characteristics of the silicon-based materials (Entwistle *et al.*, 2018).

The main objective of this study was to perform a low-cost and low-temperature synthesis of SiC for effective utilization of an agricultural waste for economically value-added product. The study also aimed to perform a doping method to narrow down the band gap using n-type dopants through the solvothermal method.

2. Methodology

2.1 Materials

Sugarcane bagasse was taken from Central Azucarera de Tarlac sugarcane mill in San Miguel, Tarlac, Philippines. Hydrochloric acid (HCl) was used to remove metal impurities and magnesium oxide came from the magnesiothermic reaction. Purchased at Chemline Scientific Enterprises, the magnesium (Mg) powder was used as the catalyst for the synthesis of SiC. Nitric acid (HNO_3) was used to remove residual silica (SiO_2) from the sample. Urea for doping was purchased at Chemline Scientific Enterprises. Distilled water was used in ensuring the cleanliness of the raw materials and the derived products. All chemicals and reagents were used without further modifications.

2.2 Preparation of Carbonized Sugarcane Bagasse

The processed sugarcane bagasse was oven-dried at 85 °C for 2 hours (h). It was then placed inside the furnace at 600 °C for 1 h under an argon atmosphere for carbonization. After firing, the sample was undergone acid treatment with 1.0 M of HCl at 100 °C for 4 h. The samples were washed with distilled water and then dry in the oven.

2.3 Preparation of SiC

The SiC was synthesized using a magnesiothermic reduction at 600 °C as described by Dasog *et al*. (2013). Briefly, magnesium powder was mixed with carbonized sugarcane bagasse (CSB) in the ratio of 1:2.5 (mass/volume). The mixed sample was heated at 600 °C for 6 h. The temperature was maintained at 600 °C to prevent the formation of intermediate Mg_2Si (Wei *et al*., 2016).

To dissolve MgO, the product was immersed in 1 M HCl solution with constant stirring at room temperature. The obtained sample was washed with distilled water and then heat-treated at 700 °C for 1 h under an air atmosphere to remove the residual carbon. Then the sample was immersed in a 50 v/v % HNO_3 solution to dissolve SiO2. Finally, the resulting sample was washed with water and dried, which obtained SiC powder as shown in Figure 1.

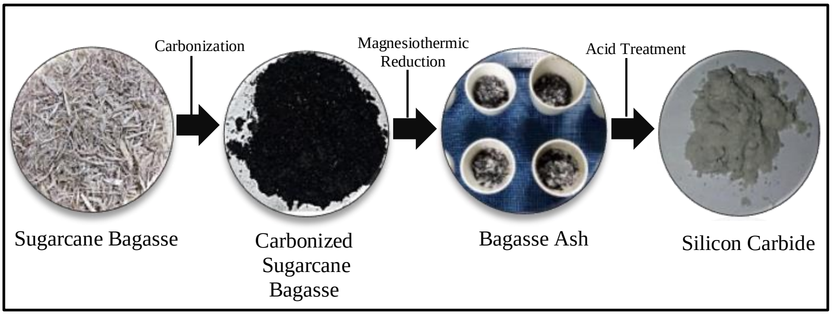

Figure 1. Schematic diagram of the synthesis of SiC

2.4 Doping of Derived SiC

The derived SiC with a high band-gap was doped via a solvothermal process with the use of n-type dopant to narrow down the band-gap of the SiC product. Urea was used as the n-type dopant. Synthesized SiC was dispersed in acetonitrile in gram-volume ratio (1:100). The dispersion was mixed with the 0.1, 1.0, 2.0 and 3.0 M dopant solution in volume ratio (1:1) and was heated at 200 °C for 10 h. After which, it was cooled to room temperature and the resulting powder was washed with distilled water. Dopant concentration was varied to determine the effect on the band-gap of the doped SiC.

2.5 Performance Assessment

Conductance experiments were done to investigate the material’s potential in solar PV cell applications. UV-Vis experiments were done to measure the band energy gap of the doped and undoped SiC. Band gap energy was calculated using the modified Planck-Einstein relation based from Dalal (2018) (Equation 1).

$$E = \frac{hc}{\lambda \times 1.60 \times 10^{-19}}\ eV \tag{1}$$

Where h is the Planck’s constant (6.626×10^{-32} J·s), c is the speed of light ($3\text{x}10^{8}$ m/s), the joule to an eV conversion factor of 1.60×10^{-19}, and λ is the wavelength with the maximum absorption of light. Performance assessment experiments revealed the possibility of SiC for PV cell application.

2.6 Characterizations and Statistical Analysis

The SiC product was characterized by scanning electron microscope (SEM) at National Analytical Services and Training Corp (NASAT) to observe the morphology of the synthesized SiC and energy dispersive X-ray (EDX) spectroscopy for elemental analysis of the SiC product. Fourier transform infrared (FTIR) spectroscopy was also carried out to identify the functional groups present in the SiC and n-doped SiC. The SiC production was carried out in three replication with four different treatments for doping. The band energy gap and conductivity measurements were done in three trials with four different treatments for doping. Least significant difference (LSD) was used to compare the difference of the means and analysis of variance – complete randomized design (ANOVA-CRD) at 95% confidence level (α = 0.05) were used to statistically analyze both the band energy gap and conductivity using Statistical Tool for Agricultural Research (STAR).

3. Results and Discussion

3.1 Synthesis of SiC

The SiC was prepared via the magnesiothermic reduction method using sugarcane bagasse as both sources of carbon and silica. Black sugarcane bagasse was produced after the carbonization. Upon addition of Mg powder and heating, the mixture in a furnace, fine and light brown colored SiC powder was obtained. SiC synthesis from sugarcane bagasse produced 66.41 and 8.56% yield of CSB and SiC, respectively. Production of carbonized sugarcane bagasse was due to the decomposition of organic species or the lignocellulose part of sugarcane into carbon. This explains the loss of mass that occurred in the carbonization.

3.2 Characterization of Synthesized SiC

The SiC, successfully produced from sugarcane bagasse through magnesiothermic reduction, had fine and smooth particles and appeared grayish in color (Figure 1).

The SEM of the synthesized SiC, as shown in Figure 2, allowed the determination of the surface morphology. The SEM showed particles in irregular shape and appeared to be crystalline in nature.

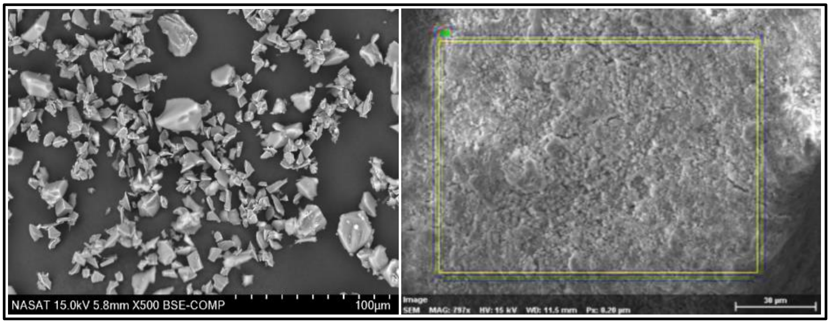

Figure 2. Surface morphology of SiC in scanning electron microscope

The EDX results (Figure 3) gave three different elemental peaks represented by three different elements in the sample, namely carbon (C) that obtained percentage value of 55.85, silicon (Si) (36.66), and oxygen (O) (7.49) by mass.

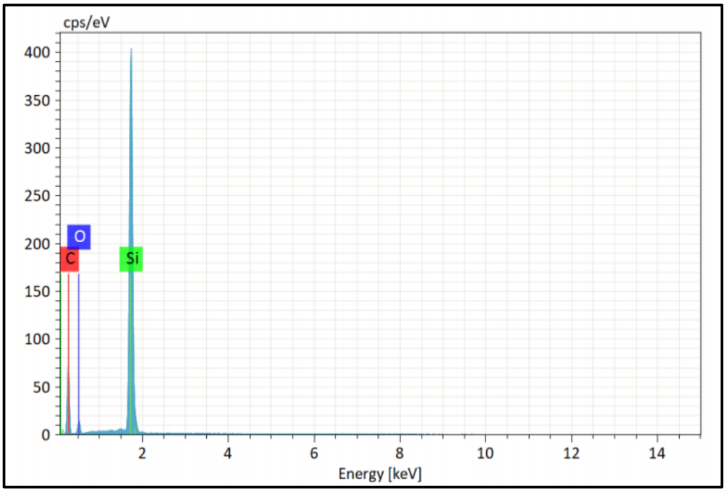

Figure 3. SEM-EDX spectra and elemental composition of the derived SiC

The results from EDX suggested that the sample has a high possibility of being SiC. It was clearly shown in the results that carbon and silicon are the dominant elements in the spectra. However, there was still silica (SiO_2) present in the sample; this was observed due to the presence of the oxygen.

In the preparation of SiC, the magnesiothermic reduction method at 600 °C was used requiring the utilization of magnesium powder as a catalyst. The EDX results showed the absence of magnesium which means that acid treatment totally dissolved the magnesium and gave a good yield. The average yield of the production of SiC from the carbonized sugarcane bagasse was 8.56%.

3.3 FTIR Spectroscopy Analysis

The infrared spectra of synthesized and urea-doped SiC are shown in Figure 4 for the identification of the functional groups present in the sample. Strong absorption peaks between 800 and 900 cm^{-1} were present in both SiC and doped SiC samples and was assigned to the stretching vibration peak of Si-C bonds (Jiang *et al.*, 2019). FTIR spectra also revealed the strong absorption peak in the region 1000 - 1200 cm^{-1}, which can be attributed to the presence of stretching vibration peak of Si-O stretching bonds (Liu *et al.*, 2017).

The strong and broad absorption peak was also observed in the region 3200 - 3600 cm^{-1} and was assigned to the presence of hydroxyl group (O-H stretching) which might be due to the excess water of the sample. C-H vibration peaks were also observed between 2800 and 3000 cm^{-1} and gave two peaks while peaks around 1600 - 1700 cm^{-1} were caused by the presence of the stretching absorption of C=C bond. This carbon-to-carbon bonding can be ascribed to the presence of excess carbon that was not totally calcinated (Larkin, 2017). Also, vibrational peaks observed in wavenumber ranging from 2300 to 2400 cm^{-1} might be due to the presence of CO_2.

FTIR spectrum for the urea-doped SiC was shown in Figure 5 and represent the changes in peaks observed after doping. For the urea-doped SiC, the peaks in derived SiC were still observed in the doped-SiC. However, in this case, the spectra became different. Since urea is an N-type dopant and a nitrogen compound, the spectra would be expected to have N-H and C-N absorption peaks. The N-H absorption peaks were observed at around 1500 - 1700 cm^{-1} and assigned as the N-H bending. The other peak was observed at 3351.56 cm^{-1} signifying the N-H stretching that overlaps to the range of O-H stretching. This is why the two bonding were located at the same spot. In addition, another peak was observed between 1400 and 1500 cm^{-1} and was assigned to be the vibrational peak of C-N bending and vibrational peak at 671.02 cm^{-1} corresponds to N-H wagging in the urea-doped SiC. From these results, it can be said that the SiC product was successfully produced and doped by urea-dopant (Table 1).

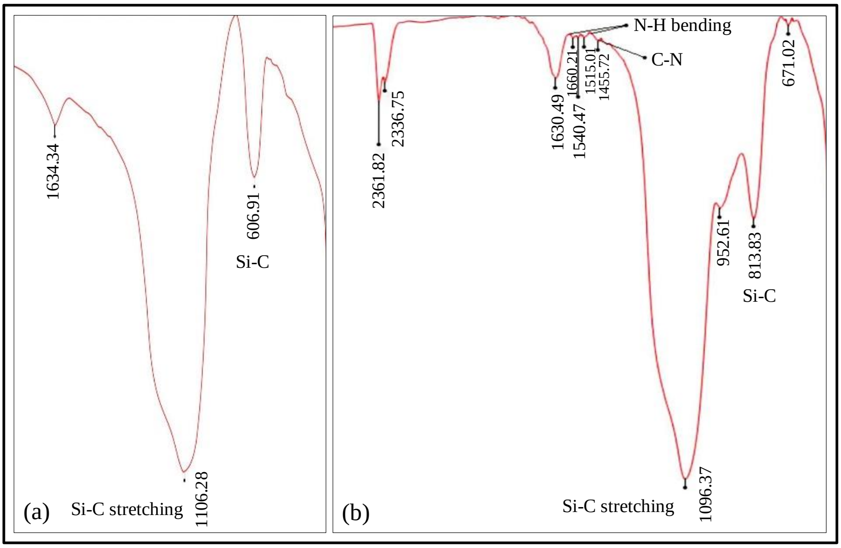

Figure 4. FTIR spectra of undoped SiC (a) and n-doped SiC (b)

Table 1. The vibrational frequency of functional groups in the FTIR spectrum of undoped and doped SiC

Wavenumber(cm^{-1})	Peak Assignment	Undoped SiC	Urea-doped SiC
600-980	N-H wagging		✓
800-900	SiC stretching	✓	✓
1000-1200	SiO stretching	✓	✓
1200-1300	Si-O-Si	✓	✓
1400-1500	C-N stretching (weak)		✓
1600-1700	C=C stretching (weak)	✓	✓
1500-1600	N-H bending		
3300-3500	O-H stretching	✓	✓

3.4 Determination of the SiC Band Gap

Optical absorption analysis using UV-Vis spectrophotometer was used to determine the peak of the λ max and to be able to calculate the estimated band-gap of the derived SiC. The peak 7 for the wavelength was observed at around 600 nm for the derived SiC that has an equivalent band-gap value of 2.07 eV (Table 2).

Table 2. Band gap energies of synthesized and doped SiC

Samples	Band-gap (eV)
Undoped SiC	$2.073^{a} \pm 0.015$
0.1 M n-type doped	$1.733^{b} \pm 0.025$
1.0 M n-type doped	$1.590^{c} \pm 0.017$
2.0 M n-type doped	$1.510^{d} \pm 0.020$
3.0 M n-type doped	$1.470^{e} \pm 0.017$

Means with the same letter are not significantly different using STAR at 5%.

Accordingly, the obtained band gap was a good built-in voltage due to its large band-gap. However, this is counter-balanced for a good semiconductor material for PV cell application which also has to absorb as much of the solar spectrum as possible with high efficiency. Therefore, a smaller band-gap is desirable. So, as a compromise, a band-gap between 1.0 and 1.7 eV makes an effective semiconductor for PV cell application (Alfonso *et al.*, 2020).

The band-gap for the urea [$(NH_2)_2CO$)]-doped SiC samples were analyzed to determine the effectiveness of doping and modifying SiC to be used in a PV cell. Results showed that doping the SiC with urea significantly decreased the band-gap energy of the SiC samples. Figure 5 shows a linear correlation between the band-gap energy and log of the concentration of dopant from 1.0 to 3.0 M.

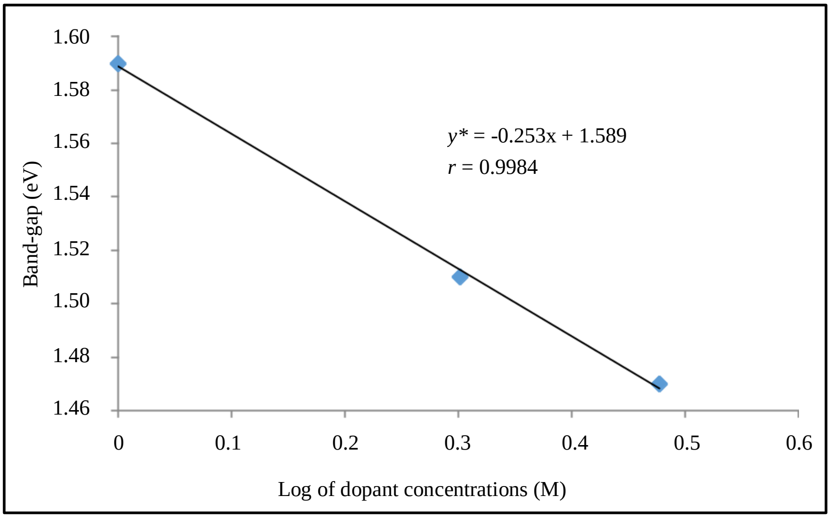

Figure 5. Relationship of band-gap (eV) and log of concentrations (M)

The equation of the line between band-gap and concentrations is shown in Figure 5, where y^* is band-gap of the derived SiC and x is the log of the concentrations.

The above equation shows a correlation coefficient $r^2 = 0.9984$ as shown in Figure 5. The graph shows three points that refer to the band-gap values that satisfy the acceptable band-gap for the PV cell. The results showed that the band-gap decreases as the concentration increases logarithmically. Statistically, it showed that the band-gap of each treatment differs significantly from each other. The mean band gap of the doped SiC samples was 1.733, 1.590, 1.510, and 1.470 eV for treatments with 0.1, 1.0, 2.0, and 3.0 M, respectively.

The results obtained for the band-gap energies related to the concentration of the dopant were in accordance with the study conducted by Patel *et al*. (2016). In addition, with decreasing band, the energy gap more free majority carriers can be trapped at this dopant band and then radiatively recombine with free minority carriers – this makes the doped-SiC as a good semiconductor material for the PV cell.

3.5 Performance Assessment of SiC

The SiC sample performances were evaluated by the conductance experiments using Nanoparticle. Since the results for the undoped SiC and 0.1 M doped SiC did not satisfy the required band gap for PV cell. The three higher concentrations were used for performance assessment.

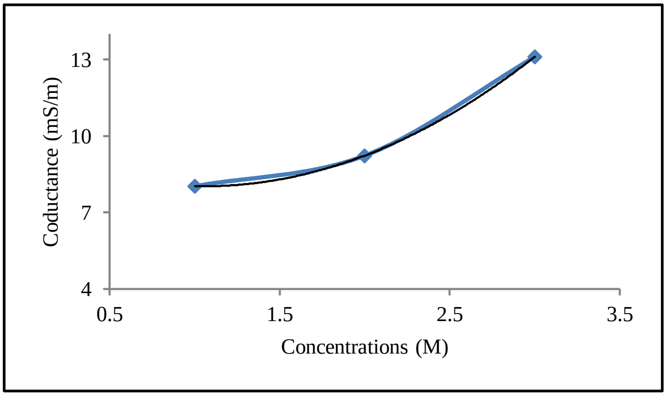

Figure 6. Relationship of conductance (mS/m) vs. concentrations (M)

Figure 6 shows the relationship between the electrical conductivity and the concentrations of the dopant which related to the empirical relationships proposed by Chabane *et al.* (2013) (Equation 2).

$$\sigma(c) = ab^{Eg(*)}M^{c}(*) \tag{2}$$

Where $\sigma(c)$ is the electrical conductivity; a, b and c are empirical constants and M stands for concentration in molarities. This equation shows that the electrical conductivity increases as the concentrations increase polynomially. Statistically, it shows that the electrical conductivity of each treatment was significantly different from each other. The mean conductance of the SiC samples were 8.03, 9.23, and 13.1 mS/m for the treatments with 1.0, 2.0 and 3.0 M, respectively. This claims the direct relation between the electrical conductivity and concentrations of the dopant suggests that the electrical conductivity of the SiC samples is predominantly influenced by the concentration (Chabane *et al.*, 2013).

4. Conclusion and Recommendation

The SiC can be synthesized from sugarcane bagasse using magnesiothermic reduction method with a yield of 8.56% having as high as 90% purity. It is supported by FTIR and SEM-EDX analysis. The band energy gap of the synthesized SiC was successfully lowered through the doping process; it tends to decrease as the concentration of the added dopant increases. Thus, the narrowed band energy gap of the SiC imparts its possibility as a material for PV cell applications.

For future studies regarding the synthesis of SiC from sugarcane bagasse via the magnesiothermic reduction method, it suggested to use other etching reagents for the improvement of the purification process. It also recommended to employ other sophisticated methods of doping material and determine the optimum concentration of dopant for the band energy gap lowering.

5. Acknowledgement

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6. References

Alfonso, A.N.R, Salazar, J.R., Monserate, J.J., & Sarong, M.M. (2020). Potential for photovoltaic cell material by green synthesis of silicon carbide from corn cob through magnesiothermic reduction. International Journal of Energy Production and Management, 5(1), 14-23. https://doi.org/10.2495/EQ-V5-N1-14-23

Aloria, M.A., Casanova, M.M., Madlangbayan, C.M., & Tan, R.V. (2017). Development and performance evaluation of sugarcane bagasse grinding and pelletizing machine for livestock feed production. Asia Pacific Journal of Multidisciplinary Research, 5(4), 126-131.

Chabane, F., Moummi, N., & Benramache, S. (2013). Experimental analysis of thermal performance of a solar air collector with longitudinal fins in a region of Biskra, Algeria. Journal of Power Technologies, 93(1), 52-58.

Chowdhury, M.S., Rahman, K.S., Chowdhury, T., Nuthammachot, N., Techato, K., Akhtaruzzaman, M., & Amin, N. (2020). An overview of solar photovoltaic panels' end-of-life material recycling. Energy Strategy Reviews, 27, 100431. https://doi.org/10.1016/j.esr.2019.100431

Dalal, M. (2018). A textbook of physical chemistry (Vol. 1.). Haryana, India: Dalal Institute.

Dasog, M., Smith, L.F., Purkait, T.K., & Veinot, J.G. (2013). Low temperature synthesis of silicon carbide nanomaterials using a solid-state method. Chemical Communications, 49(62), 7004-7006. https://doi.org/10.1039/C3CC43625J

Entwistle, J., Rennie, A., & Patwardhan, S. (2018). A review of magnesiothermic reduction of silica to porous silicon for lithium-ion battery applications and beyond. Journal of Materials Chemistry A, 6(38), 18344-18356. https://doi.org/10.1039/C8TA06370B

Larkin, P.J. (2017). Infrared and raman spectroscopy. CT, United States: Elsevier.

Liu, D., Man, J., Long, R., Gao, C., & Xiong, Y. (2017). Silicon nanostructures for solar-driven catalytic applications. Nano Today, 17, 96-116. https://doi.org/10.1016/j.nantod.2017.10.013

Luongo, G., Grillo, A., Giubileo, F., Iemmo, L., Lukosius, M., Charavin, C.A., Wenger, C., & Bartolomeo, A.D. (2019). Graphene Schottky junction on pillar patterned silicon substrate. Nanomaterials, 9(659), 1-10. https://doi.org/10.3390/nano 9050659

Jiang, S., Gao, S., Kong, J., Jin, X., Wei, D., Li, D., & Xing, P. (2019). Study on the synthesis of β-SiC nanoparticles from diamond-wire silicon cutting waste. RSC Advances, 9(41), 23785-23790. https://doi.org/10.1039/C9RA03383A

Patel, R.L., Jiang, Y.B., Choudhury, A., & Liang, X. (2016). Employing synergetic effect of doping and thin film coating to boost the performance of lithium-ion battery cathode particles. Scientific Reports 6. https://doi.org/10.1038/srep25293

Philippine Statistics Authority (PSA). (2018). Selected statistics on agriculture. Quezon City, Philippines: Philippine Statistics Authority.

Swarnakar, A.K., & Choubey, S. (2016). A short review on “Utilizing Sugarcane bagasse (SCB) – Chhattisgarh (India) prospect”. International Research Journal of Engineering and Technology, 3(8), 448-452.

Wei, X., Fan, J., Zhou, X., Shen, Y., Hu, X., & Zuo, G. (2016). Synthesis of mesoporous $Sr_2MgSi_2O_7:Eu^{2+}$, Dy^{3+} energy storage carriers using cetyl trimethyl ammonium bromide as a template. Journal of Ceramic Science and Technology, 7(4), 477-482 https://doi.org/10.4416/JCST2016-00046

Xu, Y., Li, J., Tan, Q., Peters, A.L., & Yang, C. (2018). Global status of recycling waste solar panels: A review. Waste Management, 75, 450-458. https://doi.org/10.1 016/j.wasman.2018.01.036