Biosynthesis of SnO$_2$ nanoparticles by aqueous leaves extract of *Aquilaria malaccensis* (agarwood)

Irmaizatussyehdany Buniyamin$^1$, Rabiatuladawiyah Md Akhir$^{1,3}$, Noor Asnida Asli$^{1,3}$, Zuraida Khusaimi$^{1,3}$, Mohamad Rusop Mahmood$^{1,2}$

$^1$NANO-SciTech Laboratory, Centre for Functional Materials and Nanotechnology (FMN), Institute of Science, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
$^2$NANO-ElecTronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
$^3$Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

Email: $^1$syehdany@uitm.edu.my

Abstract. Biosynthesis of tin oxide nanoparticles (SnO$_2$ NPs) was cost-effectively carried out in non-toxic aqueous mixture of *Aquilaria malaccensis* (agarwood) leaves extract and tin (IV) chloride pentahydrate solution at room temperature. The synthesized SnO$_2$ NPs were characterized by using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX) and UV-visible diffuse reflectance spectroscopy (DRS). The results from FT-IR spectra of *A. malaccensis* leaves shows the presence of functional groups of polyphenolic from bioactive compounds which act as the template for reducing and capping agents during the synthesis activity. The structural properties of the obtained nanoparticles are studied using X-ray diffraction, which indicates that the crystallite size are 6.3 and 3.4 nm for sample synthesized from extract of fresh and old leaves respectively. The morphology of the nanoparticles shows uniform distribution of agglomerated spherical nanoparticles. DRS absorption spectrum indicates the band-gap for both samples 3.23 and 3.35 eV respectively. The green synthesized SnO$_2$ NPs is suggested may play forthcoming significant roles in catalysis and optoelectronic devices.

1. Introduction
Currently nanotechnology has developed the standpoint of engineers and scientists in the direction of smart materials. Here, the study and application of miniature materials (1-100 nm) has become one of the rapid emergent research areas in wide diversity of science and engineering arenas [1]. It is known nanotechnology propose economical processes and offers a precise design and manipulation of atoms and molecules together with complete control on their exclusive properties [2]. Progression in nanotechnology has allowed researchers to manufacture various unique and improved nanomaterials, nanodevices and nanotools that applicable in many fields such as electronics, medical, pharmaceutical, aerospace, smart materials and manufacturing etc [3]. Nanomaterial owns unique size-dependent physical and chemical characteristic that are not found in bulk counterparts whereby in bulk materials, the number of atoms at the surface is less than the number of atoms in the bulk. Consequently, their
physical and chemical characteristic are typically persistent irrespective of their sizes [4]. Nevertheless, when having a size reduction of a particle to near or less than the wavelength of conduction electrons, several properties are changed as a result from the surface/volume ratio that becomes exponentially greater and the number of atom on the surface becomes substantial in accordance to the quantity of atoms in the bulk [5]. Having this beneficial prospect, researchers exploit these unique characteristic for various diverse requests and applications.

Metals and metal oxide nanoparticles displays a great request in scientific requirement such as in the chemical, electronic and pharmaceutical industries [6]. Among the nano metal oxides, tin (IV) oxide (SnO₂) an important metal oxide semiconductor with a large band energy (3.6 eV), stands as an excellent candidate for a wide range of application such as lithium-ion batteries [7,8], solar cells [9,10], catalysts for oxidation of organics matter [11–13], electrodes in solid state ionic devices [14,15], and gas sensors [16–18]. Besides, it is chemically inert, mechanically hard and thermally heat resistant [19,20]. Presently, many methods have been carried out on the synthesis of SnO₂ nanostructures such as nanoparticles, nanorods, nanotubes, nanowires, nanodisks, nanoribbons, and nanobelts [21]. Research in these areas are usually undertaken using both chemical and physical methods such as sol-gel method [22,23], hydrothermal method [24,25], high-energy ball milling [26], electrolysis [27,28], laser ablation [29–31], solvothermal [32] microwave synthesis [33] and micro emulsion [34]. Nevertheless, these methods contain several drawbacks such as application of toxic and hazardous chemicals, high temperatures and energy, and expensive to be operated [35]. Finding an alternative route as clean, non-toxic, and environmentally method has become a priority for scientist since the environment is exposed by the proposed production methods.

In recent years, green synthetic approach or biosynthesis using plant extracts have been developed to obtain a greater understanding of simplicity, environmental-friendly approach [36]. It is known to be economical and hence can be used as substitute for the large scale preparation of metal oxide nanoparticles [37]. In the green synthetic approach of SnO₂ nanoparticles (NPs), the presence of bioactive compounds such as flavonoids, alkaloids, terpenes, amino acids and carbohydrates in the plant segments, act as the reducing and capping agents that possess the key functionality on the surface morphology and size of respective product [38]. Additionally, the presence of the bioactive compounds in the system help to avoid the agglomeration between the particles [39–41]. Current progresses in plant-mediated biosynthesis of SnO₂ nanoparticles (NPs) using different types of plants and plant parts has been reported. The leaves part that involved in the biosynthesis are Daphne mucronata [42], Pruni spinosae flos [43], Calotropis gigantean [44], Brassica oleracea L. var. botrytis [45], Camellia sinensis [46], Psidium Guajava [47], Aspalathus linearis’s [48], Plectranthus amboinicus [49], Ficus carica [50] and Cleistanthus [51]. While fruit part represented plant of Ziziphus jujube [52], Lycopersicon esculentum [53], Litsea cubea [54], Citrus aurantiifolia [55], Cyphomandra Betacea [56] and Trigonelle foenum-graecum [57].

Aquilaria malaccensis, commonly called agarwood, is a highly valuable non-timber fragrant wood of Aquilaria spp. It has been used throughout different societies for medicinal, aromatic, cultural and religious purposes and can be found widely in Asia such as in Indonesia, Malaysia, China, India, Philippines, Cambodia, Vietnam, Laos, Thailand, Papua New Guinea, and Singapore [58]. A. malaccensis was reported being used for incense, fragrance and traditional medicine [59]. It is also clear from previous research undertaken that, the A. malaccensis leaves contain terpenoids, saponin, tannin, alkaloids, flavonoids, squalene, n-hexadecanoic acid, tetramethyl-2-hexadecen-1-1 and octadecatrienoic acid and several polyphenol base glucoside compounds [60–63]. There are no previous reports in the literature on synthesis of SnO₂ NPs using A. malaccensis. Toward benefit the remarkable properties of SnO₂ NPs and A. malaccensis, herein, we report the green biosynthesis of SnO₂ NPs using an extract of A. malaccensis leaves for the first time as we believed the presence of polyphenolic type compound contains in the A. malaccensis leaves would acts as the reducing and capping agent during the biosynthesis. This study was conducted using fresh and dried A. malaccensis leaves purposely to observe the effectiveness of the bioactive compounds contains in the extract towards the formation of SnO₂ NPs. This has not been previously investigated in the literature; hence, we believe the development of a plant-
mediated biosynthesis of SnO$_2$ NPs using *A. malaccensis* leaves extract will be beneficial for the enhancement structural, morphological and optical properties of SnO$_2$ NPs. The production of SnO$_2$ NPs was successfully obtained from fresh and dried leaves, with tetragonal structure whereby the smaller crystallize size of nanoparticles was obtained when using extract of dried *A. malaccensis* leaves. The synthesized SnO$_2$ NPs produced from extract of fresh and dried leaves of *A. malaccensis* was denoted as FG and OG throughout this study.

2. Experimental

2.1. Materials
Tin (IV) chloride pentahydrate (SnCl$_4$·5H$_2$O) was purchased from Sigma-Aldrich. The leaves were collected from Kuala Selangor district, Malaysia and taxonomically identified as *A. malaccensis*. Milli-Q water was used throughout the experiments.

2.2. Preparation of leaves aqueous extract of *A. malaccensis*
For the preparation of leaves extract of *A. malaccensis*, the leaves were washed using clean water. About 20 g of fresh *A. malaccensis* leaves was ground using a vegetable blender. Similar approach was performed on another batch of *A. malaccensis* leaves that being dried with similar amount. These leaves were added to separate beaker contained 100 ml of water and heated at 70°C for 20 minutes which indicated the formation of brownish colour of solution. Later, the extract was filtered using Whatman filter paper no. 1 and preserved in the refrigerator at 4°C.

2.3. Biosynthesis of SnO$_2$ NPs
The synthesis of SnO$_2$ NPs was carried out by diluting 20 ml of *A. malaccensis* leaves extract into 200 mL of water. Then it was added dropwise into 80 mL of SnCl$_4$·5H$_2$O (0.05M) solution. The formation of gelatinous solution was observed during the first 30 minutes of the reaction and the solution was continued to stir for 3 hours. The gelatinous solution was brought into centrifugation for 5 minutes (3 times) and dried in the microwave oven at 80°C for 2 hours purposely of water removal. The obtained dried powder was then crushed using mortar and pestle. Then, the calcination of the powder was carried for 3 hours at 700°C. The schematic representation of formation of SnO$_2$ NPs is illustrated in figure 1. For next characterization, the synthesized powder was crushed again in the mortar and pestle [44].

![Figure 1. Schematic representation for the synthesis of SnO$_2$ NPs using leaves aqueous extract of *A. malaccensis*.](image-url)
3. Results and Discussions

3.1. Plausible reaction mechanism of SnO$_2$ NPs

Regardless of the comprehensive idea of metal oxide nanoparticles synthesis by using plants is not fully understood until now, the bioactive compound of the plants led to the production of metal oxide nanoparticles, identical to metal nanoparticles [64]. The probable reaction mechanism of SnO$_2$ NPs is shown in figure 2. When SnCl$_4$.5H$_2$O salt solution is mixed with *A. malaccensis* leaves extract, the Sn$^{4+}$ cations dispense in the solution. Then the complex formed from the active sites of hydroxyl groups of polyphenol that is believed acting as the bioactive compound responsible for the biosynthesis activity [65]. The tetravalent Sn$^{4+}$ cation forming bridge-like network with two units of hydroxyl groups from two different chain of polyphenolic molecules. The tetravalent Sn$^{4+}$cations are believed to keep the polyphenolic molecules together that prevent agglomeration between them. The nanoparticles are obtained after the calcination of the complex.

![Diagram](image)

**Figure 2.** Plausible mechanism of SnO$_2$ NPs.

3.2. FTIR analysis

FTIR spectrum of *A. malaccensis* leaves is shown in figure 3(a). The main characteristic absorption broad band is observed at 3449 cm$^{-1}$ assigned to the presence of (O-H/NH) group, while the presence of the methyl (-CH$_3$) and methylene (-CH$_2$) aliphatic saturated (C-H) furnishes sharp asymmetric and symmetric stretching bands which can be found at 2985 and 2873 cm$^{-1}$ respectively. The carbonyl (C=O) stretching band is detected at 1738 cm$^{-1}$ attributed from the presence of carboxylic acid/ketones groups in the *A. malaccensis* leaves. The band at 1633 cm$^{-1}$ displays the presence of aromatic ring (C=C). The peak at 1431 cm$^{-1}$ is due to aromatic (C-C) stretching band. The peak at 1238 cm$^{-1}$ is due to aromatic (C-O-C) band. The (C-N) medium stretching band is observed at 1043 cm$^{-1}$ [60–63]. Since the mechanism is pointing in the role of polyphenolic compounds as the reducing and capping agent, thus by having this FTIR characterization, it evident the functional groups of the bioactive compounds (terpenoids, saponin, tannin, alkaloids, flavonoids, squalene, polyphenol etc.) in *A. malaccensis* leaves.

We have shown the FTIR spectra in figure 3(b) to confirm the formation of synthesized SnO$_2$ NPs using fresh and dried *A. malaccensis* leaves extract by highlighting the functional groups that pertinent to the desired product. The band at 3749 cm$^{-1}$ is proportional to hydroxyl group (OH) stretching vibrations associated with the water absorption on the surface of the SnO$_2$ [45]. While another existence of the OH from water molecule can be observed by the presenting band at 3200-3550 cm$^{-1}$ [66]. Strong vibration of stannous material can be observed from region within 2382 to 2720 cm$^{-1}$. This is due to the presence of hydrogen bonds involved in O-H oscillators, resulting from adsorbed water and Sn-OH group which states the functional groups of SnO$_2$ NPs [67]. Band corresponds to 1629 cm$^{-1}$ showed the presence of OH group with bending and stretching vibration, which probably originated from the water absorption during the analysis. While band within 1231 to 913 cm$^{-1}$ is agreeable with previous report that showed the metal atom commonly have absorbance within this range, whereby OG showed stronger absorbance of band that would represented higher existence of SnO$_2$ NPs [45,68].
Figure 3. (a) FTIR spectrum for untreated \textit{A. malaccensis} leaves; (b) FTIR spectra of SnO$_2$ NPs using fresh (FG) and dried (OG) \textit{A. malaccensis} leaves extract.

3.3. FESEM and EDX
The morphological feature of biosynthesized SnO$_2$ NPs was investigated by FESEM which display the morphology of agglomerated spherical-like with nanoscale diameter, extremely crystalline nature and uniformly distributed for both sample FG and OG (Figure 4). The agglomeration attributed from the action of the nanoparticle size move toward the nanoscale [69,70]. The corresponding EDX patterns show the presence of intense peaks of Sn and O which can be observed at 0.5 and 3.6 eV. The carbon impurities disappear due to high calcination temperature. The calculated weight percentages of 63.6\% O and 36.4\% Sn confirm the construction of pure SnO$_2$ phase, as evident in the EDX patterns.

Figure 4. FESEM and EDX images of biosynthesized SnO$_2$ NPs.

3.4. X-ray Diffraction analysis
The XRD pattern of the synthesized SnO$_2$ NPs as shown in figure 5 is agreeable with previous spectroscopy studies [44-46,68]. The peaks at 2\(\theta\) values of 26.5°, 33.7° and 37.8° associated with (110), (101) and (200) planes respectively that indicates the formation of SnO$_2$ with tetragonal structure according to JCPDS card no.01-077-0452. No peaks corresponding to any other phases are detected. The sharpness pattern of XRD spectrum shows that SnO$_2$ NPs are crystalline. The more pronounced and narrower peak stands for OG as indication of improved crystallinity associate with better formation of SnO$_2$ NPs by effective concentration the extract of dried \textit{A. malaccensis} leaves contained the bioactive
compound, i.e. the polyphenolic compounds. The crystallite size was found to be 6.3 and 3.4 nm for sample FG and OG respectively, calculated using Full Width at Half Maximum (FWHM) of the (110) plane using Scherrer’s formula:

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \( \text{(1)} \)

where \( \lambda \) is the X-ray wavelength of Cu Kα (1.54 Å), \( \theta \) is the Bragg’s angle, \( \beta \) is the full width at the half maximum in radians and \( k \) is unknown shape factor.

Due to the readily available bioactive compounds specifically the polyphenolic type compound contained in dried leaves of \textit{A. malaccensis}, thus the reducing and capping action occurred more efficiently, whereas the stabilization of the nanoparticles is also believed to take place which later led to the formation of smaller crystallite size of OG \[64\]. Higher flavonoids/polyphenol content was reported to be found in dried sample rather to fresh sample \[71,72\]. Besides, the formation of phenolic compounds during drying process might be due to the availability of precursors of phenolic molecules by non-enzymatic interconversion between phenolic molecules \[73\].

![Figure 5. XRD spectrum of biosynthesized SnO₂ NPs.](image)

### 3.5. UV-Vis Diffuse Reflectance Spectroscopy

The optical properties of the biosynthesized SnO₂ NPs were also investigated. Figure 6 shows the reflectance spectrum of the SnO₂ NPs whereby diffuse reflection presents in both samples. From the result, OG shows higher reflectance than FG due to smaller crystallite size and larger surface area. So as the particle size decrease, it led to decrease penetration of the incident light, which further causes less in the absorbed portion of light and increase in the reflectance \[74\].

Diffuse reflectance spectroscopy (DRS) was used to define the band-gap of the green-synthesized nanoparticles. The plot of \( (\alpha h\nu)^2 \) versus photon energy \( (h\nu) \) was obtained to determine accurate band-gap of SnO₂ NPs (Figure 7). The band-gap was analysed using the Kubelka-Munk equation:

$$\frac{K}{S} = \frac{(1 - R_s)^2}{2R_s} = F(R_s) = \alpha$$  \( \text{(2)} \)

where \( S \) is the scattering coefficient, \( K \) is the absorption coefficient, \( R = \frac{R_{\text{sample}}}{R_{\text{standard}}} \), \( R_s \) is the reflectance of an infinitly thick layer of the sample to hide the substrate and \( F(R_s) \) is the Kubelka-Munk function. The band-gap energy was obtained from the absorption spectra using the following equation:

$$F(R_s)h\nu = K (h\nu - E_g)^n$$  \( \text{(3)} \)
where $h\nu$ is the incident photon energy, and $E_g$ is the band-gap energy of the material. The exponent $n$ denotes the transition type, where $n = 1/2$, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively [46].

After the calcination process, the band-gap of samples FG and OG were found 3.23 and 3.35 eV respectively. Lower band-gap possessed by FG sample compared to OG, which displayed a low level in the carrier concentration and the existence of unoccupied electronic states [68]. The values of band-gap of FG and OG samples recommended that the biosynthesized SnO$_2$ NPs is useful for photocatalytic application.

![Figure 6. Reflectance spectrum of biosynthesized SnO$_2$ NPs.](image)

![Figure 7. A plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).](image)

4. Conclusions
In summary, the SnO$_2$ NPs were biosynthesized by using aqueous leaves extract of *Aguilaria malaccensis* (agarwood). This path is green, eco-friendly, rapid and non-toxic. The synthesis of SnO$_2$ NPs was using bioactive compounds, i.e polyphenolic type compound from *A. malaccensis* leaves which believed acts as reducing and capping agent. The FTIR analysis confirm that the presence bioactive
compounds by the presence of pertinent functional groups and the XRD shows the tetragonal structure of SnO$_2$ NPs. FESEM displays morphology of the nanoparticles with uniform distribution of agglomerated spherical nanoparticles. The DRS spectrum confirmed the biosynthesized SnO$_2$ NPs of both samples have absorption with 3.23 and 3.35 eV band-gap respectively. This finding suggests the green synthesized SnO$_2$ NPs have significant potential in catalysis and optoelectronic devices.

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References
[1] Whitesides G M 2003 *Nat Biotechnol.* 21 1161-5.
[2] Diao M S, Fromer N A, Jhon M S 2013 *J Nanoparticle Res.* 15 1-16.
[3] Khalil M, Mohamed Jan B, Tong C W and Berawi M A 2017 *Appl Energy* 191 287-310.
[4] Kim B H, Hackett M J, Park J and Hyeon T 2014 *Chem Mater.* 26 59-71.
[5] Kong X and Ohadi M M 2010 *Proc. Abu Dhabi Int Pet Exhib Conf.* (Abu Dhabi, United Arab Emirates) p 1-11.
[6] Harirprasad S, Susheela Bai G, Santhoshkumar J, Madhu C and Sravani D 2016 *Int J ChemTech Res.* 9 98-105.
[7] Zoller F, Böhm D, Bein T and Fattakhova-Rohlfing D 2019 *ChemSusChem.* 12 4140-59.
[8] Reddy M V, Linh T T, Hien D T and Chowdari B V R 2016 *ACS Sustain Chem Eng.* 4 6268-76.
[9] Wali Q, Iqbal Y, Pal B, Lowe A and Jose R 2018 *Sol Energy Mater Sol Cells* 179 102-17.
[10] Zainudin S N F, Abdullah H and Markom M 2019 *J Mater Sci Mater Electron* 30 5342-56.
[11] Prakash K, Senthil Kumar P, Pandiaraj S, Saravanakumar K and Karuthapandian S 2016 *J Exp Nanosci* 11 1138-55.
[12] Kim S P, Choi M Y and Choi H C 2016 *Mater Res Bull* 74 85-9.
[13] Srivastava N and Mukhopadhyay M 2014 *Ind Eng Chem Res.* 53 13971-9.
[14] Berenguer R, Quijada C and Morallón E 2009 *Electrochem Acta* 2009 1-9.
[15] Ko Y, Kim Y R, Jang H, Lee C, Kang M G and Jun Y 2017 *Nanoscale Res Lett.* 12 1-7.
[16] Wang B, Zhu L F, Yang Y H, Xu N S and Yang G W 2008 *J Phys Chem C* 112 6643-7.
[17] Tournier G and Pijolat C 2005 *Sensors Actuators B* 106 553-62.
[18] Tetereycz H, Kita J, Bauer R, Golonka L J, Licznierski B W, Nitsch K and Wis’niewski 1998 *Sensors Actuators B* 47 100-3.
[19] Mishra R L, Mishra S K and Prakash S G 2009 *J Ovonic Res.* 5 77-85.
[20] Gupta S, Yadav B C, Dwivedi P K and Das B 2013 *Mater Res Bull.* 48 3315-22.
[21] Roopan S M, Kumar S H S, Madhumitha G and Suthindhiran K. 2014 *Appl Biochem Biotechnol.* 175 1567-75.
[22] Aziz M, Saber Abbas S and Wan Baharom W R 2013 *Mater Lett* 91 31-4.
[23] Rachev T M and Critchlow G W 1997 *Thin Solid Films* 292 299-302.
[24] Chiu H C and Yeh C S 2007 *J Phys Chem C* 111 7256-9.
[25] Hu W and Yuan X 2017 *J Nanomater* 2017 1-7.
[26] Legendre F, Poissonnet and Bonnaillie P 2007 *J Alloys Compd.* 434-435 400-4.
[27] Rahimi R and Kurniawan F 2017 *Bull Chem React Eng & Catal.* 12(2) 281-6.
[28] He J, Cai Q Z, Xiao F, Li X W, Sun W and Zhao X 2011 *J Alloys Compd.* 509 L11-3.
[29] Gondal M A, Drmosh Q A and Salleh T A 2010 *Appl Surf Sci.* 256 7067-70.
[30] Ryzhikov A S, Shatokhin A N, Putilin F N, Rumyanseva M N, Gaskov A M and Labeau M 2005 *Sensors Actuators B* 107 387-91.
[31] Ristoscu C, Cultrera L, Dima A, Perrone A, Cutting R, Du H L, Busiakiewicz A, Klusek Z, Datta P K and Rose S R 2005 *Appl Surf Sci.* 247 95-100.
[32] He Z and Zhou J. 2013 *Mod Res Catal.* 2 13-8.
[33] Singh A K and Nakate U T 2013 *Adv Nanoparticles* 2 66-70.
[34] Zamand N, Pour A N, Housaindokht M R and Izadyar M 2014 Solid State Sci. 33 6-11.
[35] Naijar M, Hosseini H A, Masoudi A, Hashemzadeh A and Darroudi M 2020 Res Chem Intermed 46 2155-68.
[36] Gorai S 2018 J Mater Environ Sci. 9(10) 2894-903.
[37] Merlin M, Chitra S and Nalini Jayanthi N 2018 Der Pharma Chem. 10(2) 17-20.
[38] Nathan M G T and Myvizhi P 2018 Int J Pure Appl Math. 119 6439-48.
[39] Malik P, Shankar R, Malik V, Sharma N and Mukherjee T K 2014 J Nanoparticles 2014 1-14.
[40] Haritha E, Roopan S M, Madhavi G, Elango G, Al-Dhabi N A and Arasu M V 2016 J Photochem Photobiol B 162 441-7.
[41] Marshall A T, Haeverkamp R G, Davies C E, Parsons J G, Gardea-Torresdey J L and Van Agterveld D 2007 Int J Phytoremediation 9 197-206.
[42] Haq S, Rehman W, Waseem M, Shah A, Khan A R, Rehman M U, Ahmad P, Khan B and Ali G 2020 Mater Res Express 1-23.
[43] Dobrucka R, Dlugaszewska J and Kaczmarek M 2019 Inorg Nano-Metal Chem 1-10.
[44] Bhosale T T, Shinde H M, Gawade N L, Babar S B, Gawade V V, Sabale S R, Kamble R J, Shirke B S and Garadkar K M 2018 J Mater Sci Mater Electron 1-9.
[45] Osuntokun J, Onwudie D C and Ebenso E 2017 J Clust Sci. 1-14.
[46] Selvakumari J C, Ahila M, Malligavathy M and Padiyan D P 2017 Int J Miner Metall Mater. 24 1043-51.
[47] Kumar M, Mehta A, Mishra A, Singh J, Rawat M and Basu S 2017 Mater Lett 1-11.
[48] Diallo A, Manikandan E, Rajendran V and Maaza M 2016 J Alloys Compd. 681 561-70.
[49] Fu L, Zheng Y, Ren Q, Wang A and Deng B 2015 J Ovonic Res. 11 21-6.
[50] Hu J 2015 Int J Electrochem Sci. 10 10668-76.
[51] Kamaraj P, Vennila R and Arthanareeswari M 2014 World J Pharm Pharm Sci. 3(9) 382-8.
[52] Honarmand M, Golmohammadi M and Naemi A 2019 Adv Powder Technol 30 1551-7.
[53] Garrafa-Galvez H E, Nava O, Soto-Robles C A, Vilchis-Nestor A R, Castro-Beltrán A and Luque P A 2019 J Mol Struct. 1197 354-60.
[54] Hong G -B and Jiang C -J 2018 J Nanosci Nanotechnol. 18 5020-5.
[55] Senthilkumar S and Rajendran A 2017 J Nanomed Res. 6(4) 1-3.
[56] Elango G and Roopan S M 2016 J Photochem Photobiol B Biol. 155 34-8.
[57] Vidhu V K and Philip D 2015 Mater Charact. 101 97-105.
[58] Chung J P and Chen K H 2018 Plant Cell Tissue Organ Cult 1-10.
[59] Mohd Mansor A F, Abbas P, Hamdan T H, Has-Yun Hashim Y Z and Nordin A N 2017 Malaysian J Fundam Appl Sci. 540-5.
[60] Surjanto, Batubara R, Hanum T I and Pulungan W. 2019 IOP Conf Ser Earth Environ Sci. 260 1-7.
[61] Khalil A S, Rahim A A, Taha K K and Abdallah K B 2013 J Appl Ind Sci 1(3) 78-88.
[62] Lee N Y, Yunus M A C, Idham Z, Ruslan M S H, Aziz A H A and Irwansyah N 2016 IOP Conf Ser Mater Sci Eng. 162 1-6.
[63] Ito T, Kakino M, Tazawa S, Watarai T, Oyama M, Maruyama H, Araki Y, Haru H and Iinuma M J 2012 Nutr Sci Vitaminol 58 136-42.
[64] Mohamed El Shafey A 2020 Green Process Synth. 9 304-39.
[65] Gawade V V, Gawade N L, Shinde H M, Babar S B, Kadam A N and Garadkar K M 2017 J Mater Sci Mater Electron 28 14033-9.
[66] Razeghizadeh A R, Zalaghi L, Kazeminezhad I and Rafee V 2017 Iran J Chem Chem Eng. 36 1-8.
[67] Elango G, Kumaran S M, Kumar S S, Muthuraja S and Roopan S M 2015 Spectrochim Acta-Part A Mol Biomol Spectrosc. 145 176-80.
[68] Ayeshamariam A, Ramalingam S, Bououdina M and Jayachandran M 2014 Spectrochim Acta-Part A Mol Biomol Spectrosc 118 1135-43.
[69] Selvamani K, Sasiakala S and Kalaiselvi V 2018 JETIR 5(5) 947-77.
[70] Mayandi J, Marikkannan M, Ragavendran V and Jayabal P 2014 *Journals Nanosci Nanotechnol.* 2(6) 707-10.

[71] Chen M L, Yang D J and Liu S C 2011 *Int J Food Sci Technol.* 46 1179-85.

[72] Mohamad N A N, Arham N A, Jai J and Hadi A 2014 *Adv Mater Res.* 832 350-5.

[73] Que F, Mao L, Fang X and Wu T 2008 *Int J Food Sci Technol.* 43 1195-201.

[74] Liu J, Lu Y, Liu J, Yang X, Yu X 2010 *J Alloys Compd* 496 261-4.