Biogenic platinum from agricultural wastes extract for improved methanol oxidation reaction in direct methanol fuel cell

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Abstract

Platinum is the most commonly used catalyst in fuel cell application. However, platinum is very expensive, thus limits the commercialisation of fuel cell system due to the cost factor. This study introduces a biosynthesis platinum from plant extracts that can reduce the cost of platinum production compared to the conventional method and the hazardous during the production of the catalyst. The biogenic platinum was tested on a Direct Methanol Fuel Cell. Advanced biogenic of Pt nano-cluster was synthesized through a novel and facile of one-pot synthesis bio-reduction derived from natural source in the form of plant extracts as reducing agent. Several selected plant extracts drawn from agricultural waste such as banana peel, pineapple peels and sugarcane bagasse extracts were comparatively evaluated on the ability of phytochemical sources of polyphenols rich for the development of single-step synthesis for Pt NPs. Notably, the biogenic Pt NPs from sugar cane bagasse has superior electro-catalytic activity, the enhanced utilization efficiency of Pt and appreciable stability towards methanol oxidation reaction, whose ECSA value approximates 94.58 m²/g, mass activity/specific activity (398.20 mAmg⁻¹/0.8471 mA/cm²Pt) which greater than commercial Pt black (158.12 mAmg⁻¹/1.41 mA/cm²Pt).
kinetics of methanol oxidation reaction and high cost of Pt that limits DMFCs in commercial markets [4,5].

Platinum is a favourable electrocatalyst in DMFCs because of its high durability and high efficiency toward the MOR [6,7]. In past years, many attempts have been devoted to reducing the Pt loading and its cost production while concurrently persist in to intensify the immanent activity and durability of the electrocatalyst. To this end, thriving an inexpensive catalyst design with virtues enhanced activity toward the MOR and better CO tolerance for DMFCs is an effective approach to solve this problem. Many efforts have been devoted to magnifying the effectiveness of Pt electro-catalysts, such as manipulating their morphology structures, introducing support materials and alloying Pt with other metals [8]. Of all this technique is involves conventional physical and chemical methods includes thermal evaporation, pulsed laser ablation, chemical reduction, solvothermal methods, hydrothermal methods, polyol methods, electro-spinning and electro-deposition methods [9]. However, these attempts have been fraught of laborious techniques, expensive pathway, high energy consumption, lengthy reaction times, harsh reaction, low yield and biological risks. Moreover, the noxious reducing and stabilizing agents involvement are brought concern to non-biodegradability and non-biocompatibility associated with this type of synthesis consequently, may lead to hinder large-scale applications [10]. For these reasons, developing an economically and environmentally friendly method for synthesis of platinum nanoparticle using a natural resource like plant extract aqueous trough green synthesis methods is another strategy that enables to increase the efficiency of Pt electro-catalysts.

The biosynthesis of metal nanoparticles inspired from natural resources such as plant extracts happen in a single-step synthesis and one-pot reaction which offers many advantages such as that they are environmentally benign, cheap, the technique is a simple and rapid, readily scalable, they are bio-compatible, thus they eliminate hazardous reagents and multistep reaction. The metabolite compounds inside plant extracts possess fantastic functional properties as surface modifiers of nanoparticles [11]. The plant extracts is comprising of primary active metabolites such as alkaloids, phenolics, proteins, terpenoids, reducing sugar, amino acids, etc., can both functionalize as reducing agents for metal ions and capping nanoparticles to prevent agglomeration [12,10]. Thus, it is possible to utilize plant extracts in manipulating the morphology and stability of nanoparticles.

Song et al. [13] first reported platinum synthesis using plant extracts, namely the Diospyros kaki leaf extract, and obtained a > 90% Pt NPs yield at 95 °C and with a leaf broth concentration of > 10%. Zheng et al. [14] also achieved a greater 0.5 mM Pt NPs yield at 90 °C with 70% plant extract in 25 h of reaction time, and found that the biomolecules of reducing sugar, flavonoid and protein contain in Cacuminum Platycladi extract are good reducing agents for platinum ion reduction. Dauthal et al. [15] performed a rapid synthesis of Pt NPs employing Punica granatum peel extract as a template with a spherical shape and having size range of 16–23 nm. They reported that polyphenolic compounds such as ellagic acid, gallic acid, ellagic tannins and quercetin are accountable for the bio-reduction of Pt ions. Şahin et al. [16] demonstrated that Pt NPs synthesis using pomegranate extract can potentially be used for cancer treatment on human breast cancer cell line MCF-7 and showed highest inhibition of proliferation toward the cancer cell lines. It was noticed that the plant extracts carrying molecules of alcohol functional groups predominantly of the polyphenolics class and have natural antioxidant properties are potent to be exploited for redox potential along with stabilizing, growth limiting and inhibiting agglomeration, hence trigger a formation of stable complexes with Pt [17].

In this study, agriculture waste products from sugarcane bagasse (Saccharum officinarum L.), pineapple peel (Ananas comosus L.) and banana peel (Musa paradisiaca) were selected to fully realize the zero-value of residue waste to high-value functionalization material in the synthesis Pt nanoparticles. The bagasse and fruit peels are polymer complexes that mainly contain cellulose, hemicellulose and lignin, which contain aromatic and phenolic groups that make them suitable as green reducing and stabilizing agents [18]. Sugarcane has flavonoids such as apigenin, luteolin and trin derivaties, as well as compounds of high phenolic acids such as caffeic acid, sinapic acid, and hydroxycinnamic which allow antioxidant activity [19–21]. The pineapple fruit (Ananas comosus L.) is a member of the Bromeliaceae family, contains sugar, protein-digesting enzymes, bromelain, and good amounts of citric and malic acids and vitamins, which contribute to its flavour [22,23]. Bananas (Musa paradisiaca) contain high fibre and are good sources of carbohydrates, minerals and vitamins [24]. Apparently, no study has tested biogenic platinum from polyphenolic group rich plant extract as electro-catalyst in methanol oxidation reaction. Therefore, the objective of this research is to comparatively evaluate the ability of agricultural wastes from aqueous extracts like pineapple peel, sugarcane bagasse and banana peel as sources of polyphenolics for the bio-reduction of single-step synthesis for Pt NPs without the need for additional capping agents or templates, hence increasing the novelty of this study. The resulting nanoparticles were extensively characterized by their physicochemical properties using UV–VIS, XRD, TEM, FESEM-EDX, TGA-DSC and FTIR analyses. To the knowledge of the authors, there is no study that has focused on the methanol oxidation reaction using biogenic Pt NPs, therefore, the MOR is ascertained in an acidic medium and is evaluated by cyclic voltammetry analysis.

Materials and methods

All the reagents purchased were of analytical grade and were used directly. Chloroplatinic acid (H2PtCl6·6H2O) was procured from Merck. The agricultural wastes of sugarcane bagasse, pineapple peel and banana peel were collected from local crops. Methanol (C2H5OH, 99.2%) was purchased from Merck. Commercial Pt black HiSpec 1000 was obtained from Alfa Aesar.

Plant mediated extract preparation

The agricultural wastes of sugarcane bagasse, pineapple peel and banana peel were washed using tap water and cut into small pieces and were dried at 60 °C for several days. The dried peels were grinding in a commercial electric blender to obtain a fine powder and were stored in an airtight polymer plastic bag for further use. The fine powder was transferred into deionized water and was extraction at 60 °C for 30 min. The yellowish extracts were cooling at room temperature and filtered using muslin cloth and vacuum pump to separate any suspended substance and obtain the clear extracts. Meanwhile, fresh peel of Musa paradisiaca was boiled at 60 °C for 30 min without undergoing the drying process, after which it was subjected to the same process as described above. All extracts were stored in a refrigerator and were used within one week.

Green reduction of platinum nanoparticle catalyst

Pt nanoparticles were synthesized by chemical reduction using sugarcane bagasse, pineapple peel and banana peel as both reducing and stabilizer agents. The agricultural waste extracts of 10 ml were mixed with 90 ml chloroplatinic acid hexahydrate solution (1 mM) in a 1:9 ratio. The mixtures were refluxed at 95 °C and continuously stirred until colour changes from pale yellow to blackish. Then, the mixtures were sonicated for 30 min to separate the
nanoparticles from the plant extracts residue. The suspension was centrifugation at 13,400 rpm for 10 min and the recovered pellet was washed several times with deionized water and dried at 110 °C for 6 h.

Instrumentation

After the production of colloidal Pt NPs, the optical properties of the biosynthesized Pt were characterized by UV–Visible spectroscopy (Perkin Elmer, Lambda 35) in the range 200 – 800 nm. FTIR spectra of the capped functional groups of samples were measured (FTIR, Perkin Elmer, USA) in the transmittable mode over the range of 4000–400 cm\(^{-1}\) in the KBr pellets. The crystallinity and phase structures of the powdered biosynthesized Pt NPs were investigated by XRD (D8 Advance/Bruker AXS Germany) operated at a voltage of 40 kV and current of 20 mA with Cu/kα radiation (K = 1.5418 Å) with scanning range (2θ) of 20 to 90°. The elemental composition was determined by EDX equipped with a Field Emission Scanning Electron Microscope (FESEM ZEISS, Model Merlin). The morphology and structure of the powdered biogenic Pt NPs were determined via Transmission Electron Microscopy (TEM, FEI Talos L120C) operating at 120 kV. Thermal analyses and decompositions of nanoparticles were performed by a TGA/DSC Mettler Toledo 851e thermal system (STARe System, Schwerte, Switzerland) from 25 to 1000 °C at a heating rate of 10 °C/min under an inert atmosphere with open alumina crucibles containing nanopowder samples weighing approximately 10 mg.

Yield conversion of PtCl\(_6\)^2-

A 2.0 ml aliquot was taken from the reaction mixture and centrifuged at 13,400 rpm for 10 min. The upper layer of supernatant solution was taken out and re-centrifuged. About 10 ml of 5 wt% HCl solutions was added to the 1.5 ml aliquot of the resultant supernatant and diluted. The residual concentration of PtCl\(_6\)\(^2-\) was determined by an inductively coupled plasma mass spectrophotometer (ICP-MS) analyser (Thermo spectronic, USA). The conversion of Pt (IV) was calculated using the following equation:

\[
x = \left(1 - \frac{m}{195}\right) \times 100\%
\]  

where \(m\) (ppm) is the residual concentration, \(C\) (mol ml\(^{-1}\)) is the initial concentration of [PtCl\(_6\)]\(^2-\) and the coefficient 195 (g mol\(^{-1}\)) is the relative atomic weight of Pt.

Electrochemical measurement

The electrochemical analysis of biogenic Pt NPs was performed by cyclic voltammetry (CV) which were conducted in 0.5 M H\(_2\)SO\(_4\) in the presence and absence of 1.0 M methanol at a scan rate of 50
mVs$^{-1}$ in the potential window of −0.25 to 1.0 V vs. Ag/AgCl. The electrolysis cell was powered by a potentiostat/galvanostat (Autolab PGSTAT204, Netherlands) equipped with Nova 1.10 software. The instrument included a standard three-electrode system: a working electrode (glassy carbon electrode, area = 0.071 cm$^2$), a counter electrode (Pt gauze), and a reference electrode (Ag/AgCl, sat. KCl). The glassy carbon electrode (GCE) was successively refined with 0.5 and 0.05 μm α-Al₂O₃ powder and was then sonicated in water to remove the surface adsorbed particles and to ensure a mirror-like surface. About 2 mg samples of biogenic Pt NPs were dispersed into 150 μL deionized water, 150 μL 2-propanol, and 50 μL of 5 wt% Nafion® 117 solution and ultrasonically for 5 min. 2.5 μL of the dispersions were carefully drop-coated on the GCE and left overnight at room temperature. A 10 min purge interval of N₂-saturated electrolyte liquids before running the analysis and also was used throughout the experiments. A commercial Pt black was also carried out under the same conditions for comparison.

**Results and discussion**

**UV–Visible spectroscopy of biogenic Pt NPs**

Initially screening, plant extract-mediated synthesized Pt NPs were analysed using UV–Visible spectroscopy between 200 and 800 nm wavelengths. The platinum salt solution of hexachloroplatinitic acid H₂PtCl₆·6H₂O has a pale yellow colour and shows characteristic UV–VIS absorption bands around 259 nm in Fig. 1. Prior to the reduction process, a threshold peak was emitted due to Pt⁴⁺ ions and were absence after reduction complete denotes to the metallic Pt⁰ nanoparticles formation. The addition sugarcane bagasse, pineapple peel and banana peel extracts to Pt ion salt causes changes in colour from transparent light yellow to a dark, blackish colour in manners of 1.5 h, 1 h and 2 h, respectively. The pH values of the plant extracts were acidic about 3 to 3.5 for all leaf extracts. The synthesis procedure of the chemical reduction that occurs between Pt ions and plant extracts is shown in Scheme 1.

**FT-IR analysis of biogenic Pt NPs**

The natural products that were bound specifically on the surfaces of the Pt NPs were determined using FTIR analysis to identify the possible biomolecules responsible for the bioreduction and biocapping of the reduced nanoparticles. Fig. 2 shows the absorbance bands changes associated with Pt NPs synthesized by (a) Sugarcane bagasse, (b) Pineapple and (c) Banana peel extracts before and after synthesis. According to Fig. 2 (a - c), all plant extracts have very intense and broad absorption bands at 3382.6 and 2923.6 cm$^{-1}$; 3340.2 and 2918.5 cm$^{-1}$; and 3397.4 cm$^{-1}$. For sugarcane bagasse, pineapple peel and banana peel, these represent O-H stretching of the alcohol or polyhydroxy polyphenolic groups and C-H asymmetrical stretching of the methylene group, indicating the possible contribution of phenolic compounds. Medium absorption peaks around 1731.3 and 1633.6 cm$^{-1}$; 1729.2 and 1641.4 cm$^{-1}$; and 1654.4 cm$^{-1}$ could be identified as the characteristic peaks of carbonyl group C = O stretching in carboxylic acids and free amino acids N-H of amide I and amide II stretching vibrations. The observed band at 1604.8 can be assigned to the asymmetrical stretching of –COO carboxylate of proteins and alcoholic group. A medium absorption peak at 1515.2 can be attributed to the –C = C- aromatic group. The bands observed at 1455.5 and 1373.5 cm$^{-1}$ and 1375.5 cm$^{-1}$ are associated with the C-N stretching vibration of aromatic amines [25]. The peaks at 1048.8, 1162.4, 1246.5 cm$^{-1}$ and 1039.0 and 1244.6 cm$^{-1}$ were due to C-O-C stretching vibrations of ether and alcoholic groups [26]. A decrease in the peak intensities shown in the FT-IR spectrum of all biosynthesized Pt NPs after bioreduction process as compared to the spectrum FT-IR of sugarcane bagasse, pineapple and banana peel extract plants was clearly notified indicating the participation of the biomolecule functional groups in the Pt NPs synthesis. All of these peaks suggested the presence of polyphenolics, flavonoids and proteins in the plant extracts, which are responsible for the reduction of metal ions to metal nanoparticles.

**Bioreductive mechanism of Pt NPs**

Our research is focused on the power-reducing efficiency of the phytochemicals present in plant extracts, which include major polyphenolic compounds such as potential reducing agents and highly polar agents due to the abundance of polyphenolic materials in plants with high-fibre contents. The O-H and C = O groups...
showed strong abilities to bind with metal ions due to the antioxidant properties of the plant extracts [15]. The plant extracts contain various biomolecules such as amino acids, polyphenolic acids, flavonoids and reducing sugars. These biomolecules act as reducing and capping agents of Pt NPs and can also behave like ligands, and can associate along with precursor metal ions to form complexes [26]. Polyphenolic compounds and flavonoids are the potent antioxidants in plant extracts and are suggested to be likely involved in bioreduction mechanisms. According to the above findings, Scheme 2 shows a suggested mechanism for the bioreduction and stabilization of Pt-NPs using an exemplary polyphenolic compound of sugarcane bagasse extracts that have high-fiber contents.
| Plant origin                  | Conditions of synthesis | Characterisation                      | Application                  | Biomolecule                          | References |
|------------------------------|-------------------------|---------------------------------------|------------------------------|--------------------------------------|------------|
| **Piper betle L. leaf**      | 10 min Direct sunlight  | 1:9 2.1 ± 0.4 nm Monodispersed and highly stable. | Cytotoxicity and electrochemical. | Proteins.                           | [1]        |
| **Cacumen Platycladi**       | 25 h 90 N.A 2.4 ± 0.8 nm | Spherical shape. Crystalline fcc.     | N/A                          | Reducing sugar, flavonoids and protein. | [2]        |
| **Orange peel**              | 48 h 80 1:9 23 nm       | Spherical shape. Monodispersed.       | Antibacterial, Catalyst      | N/A                                  | [3]        |
| **Ocimum sanctum**           | 1 h 100 1:9 23 nm       | Irregular shape.                      | Water electrolysis.          | N/A                                  | [4]        |
| **Mentha piperita leaf**     | 2 h Calcine at 450 1:4 54.3 nm Spherical agglomerated shape. | | Electrochemical Colon cancer treatment. | Gum proteins. | [5]        |
| **Gum olibanum**             | 30 min 121 N.A 3.7–5 nm | Quasi- spherical shape. Crystalline fcc. | Colorimetric sensor.         | Proteins.                           | [6]        |
| **Azadirachta indica leaf**  | 1 h 100 1:9 5–50 nm     | Spherical shape. Polidisperse.        | Catalytic and thermal applications | Polyphenolic | [7]        |
| **Punica granatum peel**     | 30 min 90 1:4 16 – 23 nm | Spherical shape. Crystalline fcc.     | Catalyst of organic pollutant. | Proteins, flavonoids and saponins    | [8]        |
| **Taraxacum laevigatum**     | 10 min 90 1:5 2 – 7 nm  | Spherical shape. Highly dispersed.    | Antibacterial.               | Phenol, carbonyl, amide II, amine    | [9]        |
| **Maytenus royleanus leaf**  | 3 h 90 N.A 5 nm         | Spherical shape. Well dispersed.      | Anticancer for lung cancer cells and photo-catalyst. | Flavonoids, polysaccharides and proteins | [10]       |
| **Antigonon leptopus leaf, stem and root** | N.A 95 1:20 5 – 190 nm | Monodispersed spherical shape. Crystalline fcc. | N/A                          | Flavonoids, reducing sugar and phenolic acids. | [11]       |
| **Water hyacinth leaf**      | 1 h 90 1:10 3.74 nm     | Spherical shape.                      | N/A                          | Hydroxyl, nitrogen and carbohydrate groups | [12]       |
| **SO, MP, AN**               | 1 – 2 h 95 1:9 2 – 17 nm | Spherical shape. Crystalline fcc.     | Electrochemical.             | Flavonoids, reducing sugar and phenolic acids. | Present study |

*R = Reducing agent, M = metal. N.A. = Not available in literature. SO = Saccharum officinarum L., MP = Musa paradisiaca, AN = Ananas comosus L.*
and contain hydroxycinnamic acids, tricin-7-O-beta-(6'-methoxy cinnamic)-glucoside, caffeic acid and flavonoids such as apigenin. Pt4+ is first chelated through a phenolic –OH group and forms an intermediate platinum complex. Because of the high oxidation-reduction (redox) potential of Pt4+, the neighbouring phenolic hydroxyls were inductively oxidized to their respective quinones. During the bio-reduction reaction, the Pt4+ was reduced to Pt0 in the presence of free electrons or nascent hydrogen produced. The biomolecules are also adsorbed onto the surface of Pt ions, suppressing nucleated particle growth and ultimately leading to nanoparticles formation. The adjoining Pt0 atoms further collided with each other to form Pt-NPs. The Pt-NPs were further stabilized by quinones and polyphenolic acid compounds. Additionally, this bioreduction of Pt metal nanoparticles where compared to the previous works in Table 1 regarding in term of synthesizing parameters. Accordingly, the plant extract to metal ratio and molarity of reagents used in this study is very diluted with a shorter time and higher stability compared to previous work (Table 2).

**XRD analysis of biogenic Pt NPs**

Fig. 3 represent the XRD diffractogram of the crystal phase and structure of the biogenic Pt NPs. The XRD peaks of all biogenic Pt NPs synthesized by sugarcane bagasse, pineapple peel and banana peel extracts at 39.76°, 46.24°, 67.46° and 81.29°; 39.55°, 45.99°, 67.07° and 80.75°; and 39.27°, 45.97°, 67.31° and 80.90° were assigned to diffraction from the (111), (200), (220) and (311) reflections of the face centre cubic (fcc) structure of metallic platinum, respectively, which agrees well with reference to the unit cell of the fcc structure (JCPDS) file no: 00-004-0802. The (111) orientation is more intense than other peaks, indicating that (111) was very high as a prevailing orientation due to a high atomic concentration and preferential adsorption of Pt atoms on that plane during the growth process, which is considered to be a highly reactive facet and the same as d-spacing. The strong and narrow peak denotes that the product has a good crystalline nature with regard to particles. There was no discernible impurity peaks were found, showing the formation of pure crystalline platinum. The Debye Scherrer’s equation was used to calculate the crystallite particle sized corresponding to the XRD profile (Fig. 3) by utilizing the following formula (Eq. (2)) [27]:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where D is the average crystallite size, K is Scherrer’s constant (K = 0.94), \( \lambda \) is the X-ray wavelength (0.2292 nm), \( \beta \) is the full-width at half-maximum of diffraction line in radians and \( \theta \) is the half diffraction angle. The mean sizes of Pt NPs crystallite were measured using the (111), (200), (220) and (311) planes. These calculated values of approximately 7.61 nm for sugarcane bagasse, approximately 4.86 nm for pineapple and approximately 6.05 nm for banana peel extract were congruent with the measured TEM results.

**FESEM-EDX analysis of Pt NPs**

Fig. 4 (a), (b) and (c) show 3D images of the morphologies features of biosynthesized Pt NPs by field emission - scanning electron microscopy (FESEM). Regarding the plant extract type, all nanoparticles synthesized were generally polydispersed and roughly spherical in shape. Accordingly, the attribution of biomolecules such as polyphenols or antioxidants in the plant extracts were success playing the key roles in as simultaneous bio-reducing and bio-stabilizer that sustain the dispersion and distribution of NPs. However, a slightly aggregated structure was observed for all samples that maybe be due to the ‘Van der Waals’ forces during the reduction process that triggered the particles to self-assembly [28]. Furthermore, for the determination of the compositions of the biogenic Pt NPs, localized elemental information were ascertained from EDX. A high intense peak at 2 keV is present in the Pt region, which confirmed the formation of Pt NPs for all biogenic Pt NPs. Observable of low peaks for carbon and oxygen were appeared meaning that these elements coming from the phenolic group/active biomolecules from plant extracts bounded on the surfaces of Pt NPs. This supports the capping and stabilizing ability of organic moieties. The presence of O refers mainly to the formation of Pt oxide but may also be derived from the COO– group of phenolics compounds or other molecules containing C and O elements. High contents of Pt were reported from sugarcane (88.5%), followed by pineapple peel (81.0%) and banana peel (73.5%).

**Microscopic analysis of morphology structure of biogenic Pt NPs**

The TEM image further confirmed that all biogenic Pt NPs are well-dispersed and spherical shapes like presented in Fig. 5. According to Fig. 5 (a), the Pt NPs prepared using sugarcane bagasse were mainly spherical with varied in size from 2 to 17 nm with a mean size of 5 nm, which agrees well with the results obtained from FESEM images (Fig. 4 (a)). This is also close to the crystalline size of biogenic Pt NPs as estimated by Scherer’s formula and as confirmed by XRD results. The HRTEM image (see Fig. 5 (c)) as recorded exhibits lattice fringes with interplanar distance of d spacing = 0.2267 nm match with the (111) reflection of crystalline fcc phase of Pt structure. As for Fig. 5 (g), the TEM image of Pt NPs synthesized by pineapple peel have size range in 8 – 25 nm with nearly spherical shape while Pt NPs synthesized by banana peel extract have spherical shape with mean size of 3 nm. HRTEM image (see Fig. 5 (f)) illustrated for Pt NPs synthesized by banana also having the d spacing of interplanar lattice fringe of 0.2261 nm which fit with the (111) reflection of fcc structure phase of Pt in XRD diffractogram. The patterns of selected region electron diffraction (SAED) for Fig. 5(b) and 5(h) display bright circular-concentric rings consequence of the random orientations of crystal planes, indicating the crystalline phase of biogenic Pt NPs. The four rings observed in SAED images represent the diffraction planes of (111), (200), (220), and (311), whereas the SAED image in Fig. 5 (e) of biogenic Pt synthesized by banana suggested that the synthesized biogenic Pt was amorphous. In
addition, it is notable that a thin layer of biomatrix was observed in all TEM images, suggesting that the Pt NPs resided in the nanoscopic template of biomolecules present in plant extracts.

**Thermal properties**

Residual plant extracts bonded on the surfaces of the Pt NPs were assessed using TGA/DSC. Thermal degradation of the biogenic Pt NPs using plant extracts included heating from 25 to 1000 °C under an inert nitrogen atmosphere, with results shown in Fig. 6. All TGA/DSC thermograms show similar thermal decomposition trends with two stages. The first decomposition stage occurs is the desorption of water while the second stage involves the thermal degradation biomolecule compounds bounded on the surface of biogenic Pt NPs [25]. A small total weight loss of –8.64% occurs for the Pt NPs synthesized by sugarcane bagasse while total weight losses of –14.75 and –22.85% occur for the Pt NPs synthesized by pineapple peel and banana peel, respectively. These stipulate the existence of small amounts of impurities and organic residue in the Pt NPs synthesized by the plant extracts. The initial weight loss that occurs during the first decomposition step of all biogenic Pt NPs up to 156 °C is the removal of strongly coordinated water molecules via the condensation of hydroxyl with external water molecules. The transition is supported by the appearance of an endothermic DSC peak at approximately 140 °C. Then, the Pt NPs show steady weight loss beginning at 150 °C, with thermal decomposition ending at 800 °C, which due to the decomposition of organic compounds that is most likely resulting from the surface desorption of the organic compounds present in the nanoparticle powder. Slight, further degradation was observed in thermogram of the Pt NPs synthesized by banana peel extract, but no further degradation was observed after 800 °C for the Pt NPs synthesized by sugarcane bagasse and pineapple extracts resulted in a nearly horizontal curve, which suggests the stability of elemental platinum. The thermo-gram of all biogenic Pt NPs exhibited excellent thermal stability.
Assessment of electrochemical properties of synthesized biogenic Pt NPs

H₂ adsorption and desorption

The electro-catalytic activity of all biogenic Pt NPs was studied in an acidic medium by voltammetric measurements at room temperature with a saturated N₂ purge during the experiments. Fig. 7 (a) and (b) show the cyclic voltammograms (CVs) normalized to catalyst loading and the geometric area of the working electrode. The typical CV curve used to determine the hydrogen and oxygen absorption on all catalysts were evaluated in 0.5 M H₂SO₄ at scan rate of 50 mV s⁻¹ in the potential window of −0.25 to 1.0 V vs Ag/AgCl at room temperature to quantify the ECSA values of different catalysts. The ECSA values of the respective catalysts calculated from the integrated charge area under the hydrogen adsorption peak, which represents the total charge (Q_H) after deducting the area that corresponds to double-layer charging in the CV, using below equation [29]:

\[
\text{ECSA (m}^2\text{g}^{-1}) = \frac{Q_H (\text{C m}^{-2})}{2.1 (\text{C m}^{-2}) \times [\text{Pt}] (\text{g m}^{-2})}
\]

where Q_H is the charge for hydrogen adsorption (C m⁻²), [Pt] represents the platinum loading (g m⁻²) on the working electrode and 2.1 (C m⁻²) is the charge required to oxidize a monolayer of H₂ onto the Pt surface.

From Fig. 7 (a), the voltammogram reveals information associated hydrogen adsorption/desorption area and the oxide formation/reduction area on the Pt NPs surfaces. As observed, the CVs show strong characteristics of hydrogen absorption/desorption peaks below approximately 0.25 V and Pt oxidation/reduction peaks beyond approximately 0.4 V. The higher potential peak at approximately 0.56 V is associated to the Pt-oxide reduction (Pt + H₂-O → Pt-OH + H⁺ + e⁻ [30]) on the biogenic Pt NPs surface during a forward scan (anodic sweep) [31]. The characteristic peak at lower potential in the −0.25 to 0.1 V region is the monolayer hydrogen adsorption/desorption on the Pt NPs active surface. The calculated ECSA value for Pt NPs-sugarcane bagasse was 94.58 m²g⁻¹, which is much higher than those of Pt NPs-banana peel extract (3.69 m²g⁻¹), Pt NPs-pineapple peel extract (1.69 m²g⁻¹) and commercial Pt black (27.49 m²g⁻¹). However, the hydrogen adsorption and desorption regions in the CV of Pt NPs-banana and Pt NPs-pineapple were very small, suggesting that the organic...
molecules may block the active sites of the Pt particles. In addition, other contributing factor is may be due to the limited interaction during bio-reduction between platinum precursors with plant extract of pineapple peel extract and banana peel extract and lack of sufficient functional groups that lead to un-complete reduction. This order is similar to findings reported by Prabhuram et al. [32] and Guo et al. [33], who noted no characteristic features associated with hydrogen absorption/desorption due to the complete blocking of Pt active sites by surfactant molecules.

The biogenic Pt NPs-sugarcane exhibited a dramatically superior ECSA, approximately 3.44 times that of commercial Pt black, demonstrating a significantly improved electrochemical activity on Pt NPs synthesized by plant extracts. It seems that more active sites are available for H₂ absorption/desorption and help improve the electro-oxidation of the methanol reaction. The higher ECSA value is attributed to the presence of well-dispersed and very fine Pt particles, as illustrated in the TEM image resulting from functionalized active biomolecules from plant extracts. The particle sizes also play in the catalyst's catalytic activity as most of the chemical reactions occur on the catalyst's surface; therefore, decreasing particle size leads to an increase in catalytic activity [34]. The uniform size and good dispersion of Pt nanoparticles is thought to produce a larger accessible surface area of active site, thus promoting a higher catalytic activity than aggregated nanoparticles. Furthermore, the onset potential (E_{onset}) Pt NPs of all plant extracts are shifted to negative potential in accordance of 0.203 V ≤ 0.205 V < 0.278: Pt NPs-banana peel extract ≤ Pt NPs-pineapple peel extract < Pt NPs-sugarcane compared to Pt black commercial of 0.313 V.

Methanol oxidation reaction

The electrocatalytic performance toward the methanol electro-oxidation for all biogenic Pt NPs (Pt NPs - sugarcane, Pt NPs - banana peel extract, Pt NPs - A. comosus pineapple peel extracts) and commercial Pt black were evaluated by the CVs in 0.5 M H₂SO₄ + 1.0 M CH₃OH. Fig. 7 (b) clearly shows the CV curves of forward anodic peaks and reverse cathodic peaks for different biogenic electro-catalysts for methanol oxidation. The oxidation peak in the forward scan at the range of about -0.65 – 0.84 V is the characteristic peak for methanol oxidation on the Pt surfaces with the formation of carbonaceous intermediate such as CH₂OH_{ads}, CHOH_{ads}, CHO_{ads} and the strongest adsorbed CO species, and species will oxidized to Pt-OH and Pt-O species at higher potential [35]. Whereas the reverse scan peak emerged at a range of about -0.4 – 0.67 V corresponds to the efficiency of the removal of carbonaceous species that were generated during the forward scan of methanol oxidation. Generally, as described by others, possible oxidation reactions of the methanol are as follow [4]:

\[
\text{Pt} + \text{CH₃OH} \rightarrow \text{Pt} - (\text{CH₂OH})_{ads} \quad (4)
\]
\[
\text{Pt} - (\text{CH₂OH})_{ads} \rightarrow \text{Pt} - (\text{CH₂OH})_{ads} + \text{H}^+ + e^- \quad (5)
\]
\[
\text{Pt} - (\text{CH₂OH})_{ads} + \text{Pt} \rightarrow \text{Pt}_2 - (\text{COH})_{ads} + \text{H}^+ + e^- \quad (6)
\]
\[
\text{Pt}_2 - (\text{COH})_{ads} + \text{Pt} \rightarrow \text{Pt}_3 - (\text{CO})_{ads} + \text{H}^+ + e^- \quad (7)
\]
\[
\text{Pt} - (\text{CO})_{ads} \rightarrow \text{Pt} - (\text{CO})_{ads} + \text{H}^+ + e^- \quad (8)
\]
\[
\text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt} - (\text{H}_2\text{O})_{ads} \quad (9)
\]
\[
\text{Pt} - (\text{H}_2\text{O})_{ads} \rightarrow \text{Pt} - (\text{OH})_{ads} + \text{H}^+ + e^- \quad (10)
\]
\[
\text{Pt} - (\text{COH})_{ads} + \text{Pt} - (\text{H}_2\text{O} \text{ or } \text{OH})_{ads} \rightarrow 4\text{Pt} + \text{CO}_2 + 3\text{H}^+ + 3e^- \quad (11)
\]
\[
\text{Pt} - (\text{H}_2\text{O})_{ads} + \text{Pt} - (\text{CO})_{ads} \rightarrow 2\text{Pt} + \text{CO}_2 + 2\text{H}^+ + 2e^- \quad (12)
\]
\[
\text{Pt} - (\text{OH})_{ads} + \text{Pt} - (\text{CO})_{ads} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + e^- \quad (13)
\]

The total electro-oxidation of methanol is expressed as:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^- \quad (14)
\]

As shown in Fig. 7 (b), biogenic Pt NPs- sugarcane had the highest mass activity of 398.20 mA/mgPt compared to the other two biogenic Pt NPs and was 2.52 times greater than that of commercial Pt black (158.12 mA/mgPt). The onset potential (E_{onset}) of

Fig. 6. TGA/DSC termogram of synthesized biogenic Pt NPs of (a) Saccharum officinarum L, (b) Ananas comosus L and (c) Musa paradisica aqueous broth extract.
methanol oxidation given by all biogenic Pt NPs show shifts to more negative values with following order: Pt NPs-banana peel extract (0.203 V) < Pt NPs-pineapple peel extract (0.205 V) < Pt NPs-sugarcane bagasse (0.278 V) than commercial Pt black (0.313 V), which means that faster of methanol oxidation reaction can happen where it only require lower potential to perform. The Pt NPs-sugarcane bagasse displayed the highest current density at approximately ~0.84 V vs Ag/AgCl in anodic sweep and at approximately ~0.67 V vs Ag/AgCl in a cathodic sweep. These results are reflected to the electrocatalytic activity of the catalyst which strongly demonstrated the enhancement of catalytic activity of the Pt NPs in MOR synthesized using green chemical reduction from plant extracts.

According to histogram in Fig. 7 (d), further analysis on efficiency utilization of Pt mass can be investigate from the specific activity (mA/cm² Pt) where Pt NPs-sugarcane bagasse displayed remarkable high mass activity approximately 398.20 mA/mg with small amount utilization of specific activity (mA/cm² Pt) approximate 0.84711 mA/cm² Pt as compared to others Pt electro-catalyst where using high utilization of Pt mass accordingly to the specific activity.

Table 3
Comparison of the electrochemical activities of biosynthesizes Pt NPs and commercial Pt black towards MOR.

| Catalyst                     | ECSA (m²/g of Pt) | Peak potential (V vs Ag/AgCl) | Onset potential (V vs Ag/AgCl) | Mass activity (mA/mgPt) | Specific activity (mA/cm² Pt) | Peak current density (mA/cm²) | CO tolerance | I₂/I₁ ratio |
|------------------------------|-------------------|--------------------------------|--------------------------------|-------------------------|------------------------------|-------------------------------|--------------|-------------|
| Pt Saccharum officinarum L.  | 94.58             | 0.844                          | 0.278                          | 398.20                  | 0.847                        | 87.68                          | 0.81         |             |
| Commercial Pt black         | 27.49             | 0.801                          | 0.313                          | 158.12                  | 1.410                        | 50.48                          | 0.79         |             |
| Pt Musa paradisiaca         | 9.91              | 0.681                          | 0.203                          | 37.56                   | 2.048                        | 4.985                          | 0.94         |             |
| Pt Ananas comosus L.        | 1.69              | 0.644                          | 0.205                          | 2.52                    | 0.360                        | 0.609                          | 0.83         |             |

Fig. 7. (a) Represent the H₂ absorption and desorption of Pt catalyst in 0.5 M H₂SO₄ electrolyte at 50 mV/s; (b, c) CV curves in 0.5 M H₂SO₄ and 1.0 M CH₃OH aqueous at 50 mV/s and (d) histogram of mass activity and specific activity for biogenic electrocatalyst Pt NPs.
This study highlighted the high performance of Pt NPs-sugarcane bagasse extract in methanol electro-oxidation (MOR) with the following characteristics:

- **Peak Potential (V vs Ag/AgCl)**: 0.84 V
- **Peak Current Density (mA/cm²)**: 87.68 mA/cm²
- **Specific Activity (mA/mg Pt)**: 398.20 mA/mg

Comparing the results to other studies, Table 4 summarizes the overall performance of the synthesized catalysts based on the CV analysis and evaluation between the regions of methanol oxidation potential in acidic media.

### Table 4: Comparison of Methanol Electro-oxidation on Various Methods

| Catalyst Type | Type of Catalyst and Morphology | Synthesis Methods | ECSA (m²/g of Pt) | Peak Potential (V vs Ag/AgCl) | Peak Current Density (mA/cm²) |
|---------------|--------------------------------|-------------------|------------------|-------------------------------|-------------------------------|
| This study    | Pt cluster                     | Biosynthesis using plant | 94.58 m²g⁻¹      | 0.84                          | 87.68 mA/cm²                  |
| Kong et al.   | Pt sponge-like                 | Photochemical synthesis | 31.73 m²g⁻¹      | 0.73                          | 340 mA/mg                     |
| Shi et al.    | Pt/Pd sheet-assembled network | Conventional wet-chemical reduction | 38.65 m²g⁻¹ | 0.95                          | 266 mA/mg                     |
| Qian et al.   | Pt needle-flower like          | Electrodeposition   | 0.42 cm²         | 0.64                          | 87.7 mA/mg                    |
| He et al.     | PtAu stellated morphology     | Conventional wet-chemical reduction | 64.2 m²g⁻¹  | –                             | 48.03                         |
| Han et al.    | CuPt stellated morphology     | Seed-mediated       | 42.1 m²g⁻¹       | 0.61                          | 0.73                          |
| Wang et al.   | Pt nanosponge foil            | Conventional wet-chemical reduction | 25.98 m²g⁻¹ | 0.85                          | 192.02 mA/mg                  |
| Yang et al.   | PtPd porous nanostructure     | Polyol reduction    | 31.59 m²g⁻¹      | –                             | 210.35 mA/mg                  |
| Yang et al.   | PtPd hollow                   | Galvanic replacement reaction | 19.7 cm²      | 0.7                           | 346.8 mA/mg                   |
| Li et al.     | PtAg octahedral               | Hydrothermal        | 57.48 m²g⁻¹      | –                             | 372.3 mA/mg                   |

**Conclusion**

The present study is the first of its kind that presents the preparation, characterization and chemical activities of biogenic Pt NPs and their catalytic properties toward the methanol oxidation reaction for fuel cell applications. This paper presents a novel, one-pot facile synthesis and environmentally benign to prepare a novel biogenic Pt nano-clusters electro-catalyst through bio-reduction functionalized by active biomolecules present in plant extracts and comparing the results to other studies of reducing agents in chemical bior-eduction methods. Pt NPs-sugarcane bagasse extract exhibited the most enhanced ECSA, mass activity and efficient Pt mass utilization for the MOR relative to other Pt NPs plant-mediated synthesis (Pt NPs-M. paradisiaca and Pt NPs-A. comosus L.) and to commercial Pt black. It presented the highest ECSA as 94.58 m²/g and greater specific (mass) activity as 398.20 mA/mg. This may be attributed to the highly dispersed and uniform size of Pt NPs effects from the stabilizing and functionalized effect of functional organic molecules inside the plant extract of sugarcane bagasse and more active reaction sites in the morphology/structure were exposed, in which the smallest particle sizes will provide a larger surface area, leading to kinetic activity in methanol oxidation reaction. This facile one-pot synthesis obviously offers a new strategy for high-performance DMFCs and reduces the strategy cost of production.

**Declaration of Competing Interest**

The authors declared that there is no conflict of interest.

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**Appendix A. Supplementary material**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jare.2020.06.025.
