THE EFFECT OF CARBON DOTS ON CONDUCTIVE INK AS A VITAMIN C ELECTROCHEMICAL SENSOR

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THE EFFECT OF CARBON DOTS ON CONDUCTIVE INK AS A VITAMIN C ELECTROCHEMICAL SENSOR

by

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LIST OF SYMBOLS

Symbol	Description	Unit
R	Measured resistance	Ω
Rs	Sheet resistance	Ω/sq
ρ	Resistivity	Ω·cm
W	Width	cm
L	Length	cm
t	Average thickness	cm

LIST OF ABBREVIATION

CA	Citric acid
CB	Carbon black
CDB	Carbon dots blended
CDs	Carbon dots
CDS	Carbon dots on surface
CI	Commercial Ink
CV	Cyclic voltammetry
DH	Degree of hydrolysis
LOD	Limit of detection
LOQ	Limit of quantitative
MW	Molecular weight
PBS	Phosphate buffer solution
PE	Printed electronics
PMMA	Poly(methyl) methacrylate
PVA	Polyvinyl alcohol
SEM	Scanning electron microscope
SPE	Screen-printed electrode

KESAN DOT KARBON TERHADAP DAKWAT KONDUKTIF SEBAGAI SENSOR ELECTROKIMIA VITAMIN C

ABSTRAK

Permintaan untuk sensor electrokimia mudah alih dan boleh dibuang menggunakan dakwat konduktif semakin meningkat kerana kelenturan dan kekonduksiannya. Dengan penemuan dot karbon baru-baru ini dengan peningkatan kekonduksiannya, ia dapat diubahsuai sebagai bahan tambahan untuk melihat kesannya sebagai sensor elektrokimia terhadap vitamin C. Dalam penyelidikan ini, pembuatan jalur sensor tanpa substrat yang senang dan murah menggunakan karbon hitam (CB) sebagai pengisi dan pelbagai pengikat seperti polivinil alkohol (PVA) dan polimetil metakrilat (PMMA) telah dihasilkan. Dakwat konduktif disiapkan dengan melemparkan pada kain tanpa tenunan menggunakan alat pemutus membran dan dibiarkan sembuh. Kemudian, ia dipotong dalam ukuran yang sama untuk pencirian dan analisis voltammetri siklik (CV) bagi pengesanan vitamin C. Komposisi dakwat konduktif yang terbaik ialah 6:4 (m:m) CB:PVA dengan berat molekul (MW) dan tahap hidrolisis yang tinggi. Pautan silang PVA tidak diperlukan kerana ini akan mengurangkan kekonduksian dakwat. Rintangan terendah diperoleh untuk jalur sensor CB/PVA dan CB/PMMA ialah $0.357 \pm 0.03\ \Omega\cdot cm$ and $2.735 \pm 0.2\ \Omega\cdot cm$ menunjukkan dakwat konduktif CB/PVA lebih berpotensi daripada dakwat konduktif CB/PMMA and dakwat komersial. Pengadukan dot karbon (CDs) dapat menurunkan rintangan pada jumlah optimum. Walau begitu, jalur CB/PVA tidak dapat menghasilkan puncak pengoksidaan dan penurunan dalam CV, menunjukkan ketidakan responsif terhadap pengesanan vitamin C sementara jalur sensor CB/PMMA dapat mengesan kewujudan vitamin C dengan had pengesanan (LOD) 0.622 mM dan julat linear dalam 5 – 15 mM. CDs juga dilapiskan pada permukaan jalur sensor CB/PVA dan CB/PMMA tetapi

hanya melekat pada permukaan CB/PMMA disebabkan oleh struktur berliang jalur sensor CB/PMMA sementara telah tanggal daripada permukaan CB/PVA. CDs yang dilapiskan telah berjaya menurunkan rintangan sehingga 36% untuk kedua-dua jalur sensor dan meningkatkan arus belakang CB/PMMA dalam analisis CV menunjukkan peningkatan kekonduksian. Walau bagaimanapun, arus puncak pengoksidaan menurun disebabkan reaksi tolakan cas negative yang sama pada vitamin C dan kumpulan karboksil CDs. Oleh it, tambahan CDs hanya sesuai untuk pengesanan analit cas positif. Jalur sensor yang dihasilkan menunjukkan kestabilan yang baik dengan 10-kitaran CV analisis dalam keadaan neutral dan berasid tetapi kurang sedikit dalam keadaan alkali.

THE EFFECT OF CARBON DOTS ON CONDUCTIVE INK AS A VITAMIN C ELECTROCHEMICAL SENSOR

ABSTRACT

The demand for portable and disposable electrochemical sensors using conductive ink is increasing due to its flexibility and conductivity. With the recent discovery of carbon dots and its conductivity improvement, it can be modified as an additives in the conductive ink to see its effect as an electrochemical sensor towards vitamin C. In this study, an easy and inexpensive fabrication of unsupported sensor strips using carbon black (CB) as filler and alternate different binder such as polyvinyl alcohol (PVA) and polymethyl methacrylate (PMMA) was fabricated. The conductive ink prepared was casted on non-woven cloth using membrane casting tool and allowed to cured. It was then cut into standard sizes for characterization as well for cyclic voltammetry (CV) for vitamin C detection. The optimum of the conductive ink was 6:4 (m:m) CB: PVA, with higher molecular weight (MW) and hydrolysis degree (DH) of PVA. Crosslinking of PVA was not needed as it will decrease the conductivity of the ink. The lowest resistivity obtained for CB/PVA and CB/PMMA sensor strips were 0.357 ± 0.03 Ω·cm and 2.735 ± 0.2 Ω·cm which show CB/PVA conductive ink has more potential than CB/PMMA conductive ink and even commercial ink. The blending of carbon dots (CDs) was able to decrease the resistivity at optimum amount. However, CB/PVA sensor strip was not able to produce any oxidation and reduction peak in CV showing its non-responsiveness towards detection of vitamin C while CB/PMMA sensor strip was able to measure the vitamin C presence with limit of detection (LOD) of 0.622 mM and linear range of 5 – 15 mM. CDs was coated on CB/PVA and CB/PMMA sensor strips surface but only adhere to CB/PMMA which may due to porous structure of CB/PMMA sensor strip while detaching of CDs observed for

CB/PVA. The CDs coated on the surface was able to decrease the resistance up to 36% for both sensor strips and increase the background current of CB/PMMA CV response showing improved conductivity. However, the peak current response decreased due to repulsion reaction of same negative charge of vitamin C and the carboxyl groups on CDs surface. Therefore, the CDs modification was deduced only suitable for detecting positive charge analyte. The proposed sensor strips exhibited great stability with a 10-cycles CV run in neutral, acidic but decent performance in alkaline condition.

CHAPTER 1 INTRODUCTION

1.1 Background

Conductive ink is an ink that able to conduct electricity with either conducting metal nanoparticles, (Fernandes et al., 2020a; Z. Wang et al., 2016) polymer nanocomposite (Kazemzadeh Farizhandi et al., 2020; H. Liu et al., 2018), or carbon-based nanomaterials as the composition of the ink (Karagiannidis et al., 2017; Phillips et al., 2017; Saidina et al., 2019). They are mainly used for the printed electronics industry to produce flexible and light-weight printed electronics (PE) such as radio frequency identification tags (RFID) (Amendola et al., 2018; Leng et al., 2019), capacitor (McKerricher et al., 2015), printed circuit, motion sensor (Ko et al., 2018) due to their desired properties. Their properties of light weight, low-cost, high-throughput, eco-friendly and easy fabrication make them as their advantage for recent development and extensive research in the electrical field.

Printed electronics (PE) refers to the electronic devices fabricated using printing technologies with a variety of substrate for conductive ink to be printed on. A substrate such as paper, resins, plastics or polymer can be utilized to produce flexible electronics. Compared to conventional electronic devices mainly made from silicon (Si) as raw materials, the manufacturing of conventional electronic devices depends on photolithography and vacuum techniques which require clean room facilities and result in high cost. In the end, they are more expensive and even create problem when comes to disposal and waste issues (Song et al, 2019). On the other hand, PE offers cost-effective way and higher speed of fabrication. Besides, by using eco-friendly substrate and materials, PE become disposable waste which do not harm the environment.

The PE market is projected to grow from USD $7.8 billion in 2020 to U.S.$ 20.7 billion by 2025 with a Compound Annual Growth Rate (CAGR) of 21.5% taking

account into the Covid-19 impact. Development of smart and connected devices drive the growth of the market, which often require energy-efficient, thin and flexible consumer electronics. With the current on-going Covid-19 pandemic, it reduces human labour in which human labour is highly required by the display industry. The reduction of orders, shortage of labour and ceasing of operation cause significant effect in the PE market. However, with the increasing of demand of Internet of Things (IoT) in the 21st century, the PE market is closely related since the adaptation of wearable devices, convenient, smart packaging and medical wearables are starting to progress (MarketsAndMarkets, 2020). **Fig. 1** shows the application of printed electronics in various fields in China up to 2020 and forecast up to 2025. The demand for PE in the display is the highest, followed by photovoltaic, which is the solar panel, then lighting, RFID and others. Printed sensor market which is considered as a type of PE was valued at USD 8.63 billion in 2019, at a CAGR of 6.62% during the forecast period of 2020 – 2025 in market report from Mordor Intelligence (Mordor Intelligence, 2019). Lesser cost is needed for the printed sensors technology and can be manufactured on large scale, providing high economies of scale to manufacturers. As printed sensor emerged in the market, it offers capabilities that are unavailable in the conventional silicon sensor system, which offer flexible form due to low profiles and bendable substrates with rapid responses to stimuli. The material cost can be saved by combining the sensors with the measurement system on a single substrate. Asia Pacific is expected to hold the largest market for printed sensor. Thin Film Electronics ASA, located in United States recently signed a distribution agreement with CymMetrik, a Chinese company for expansion of sales, particularly in China, Taiwan, India and other Asia-Pacific nations. The regional growth rate is shown in **Fig. 2**.

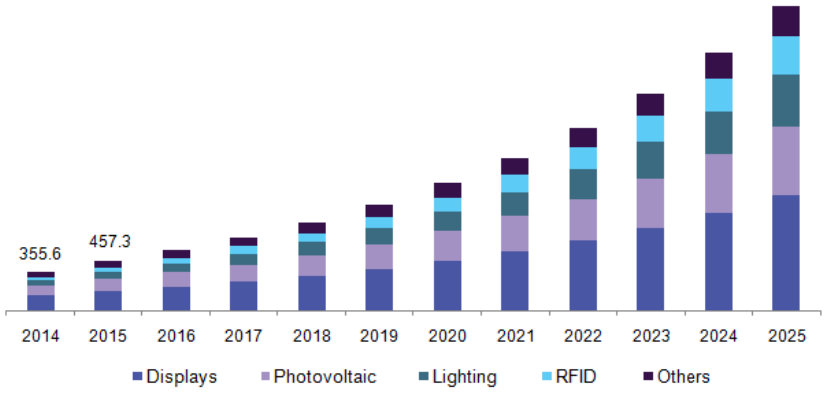

Fig. 1 China printed electronics by device, 2014 - 2025 (USD Million) (MarketsAndMarkets, 2020.)

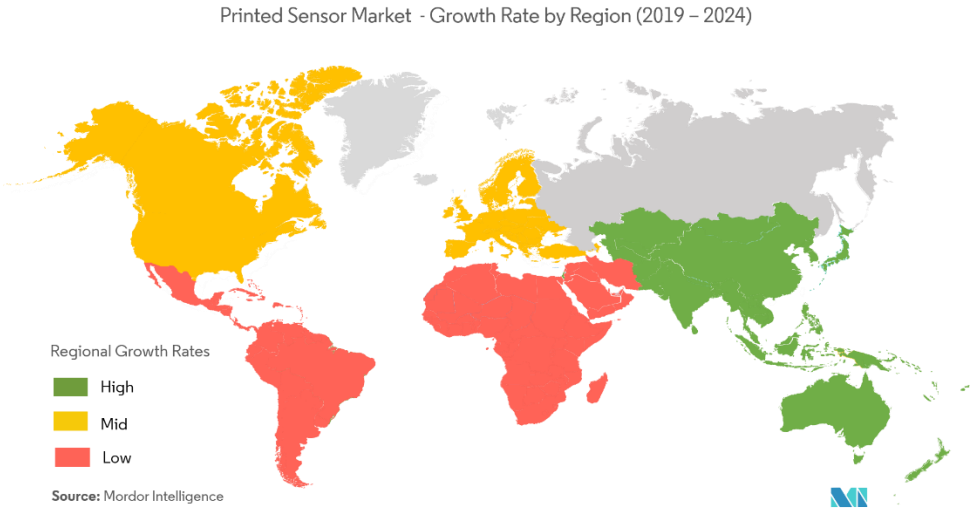

Fig. 2 Regional growth rate of printed sensor

There is a lot of carbon-based conductive ink by using carbon source such as graphene (Man Song, 2019), graphene nanosheet (Jiang et al., 2018), graphite (Phillips et al., 2017), carbon black (Lixin Liu et al., 2021), carbon nanotubes (Shin et al., 2016) and multi-walled carbon nanotubes (Ko et al., 2018), or a hybrid of them. They can be made into electrochemical sensors which combine high sensitivity and simplicity and apply in clinical, environmental, food and industrial analyses (Dakshayini et al., 2019). With various printing technologies such as screen printing, inkjet printing, gravure printing and flexography, Inkjet printing is a well-established printing technique which is simple and easy to use compared to other printing technologies. **Fig. 3** shows the most

frequently used printing technologies in a global where screen printing is most commonly applied followed by inkjet printing. Inkjet printing is a printing technique where the ink is filled in the ink cartridge and equipped into a printer. Desired shape was drawn with software, which connected to the printer to print the shape. With this printing technique, these carbon-based conductive inks can be made into the disposable electrochemical sensor for single use, which is a type of printed electrode (PE) and can be found in most industries now for sensing application (Araújo et al., 2020a). These PE come to attention since it is low cost and easy to fabricate. However, some disposable PE has created environmental pollution due to the toxicity properties of carbon-based materials Therefore, further research is required to overcome these problems for long-term production.

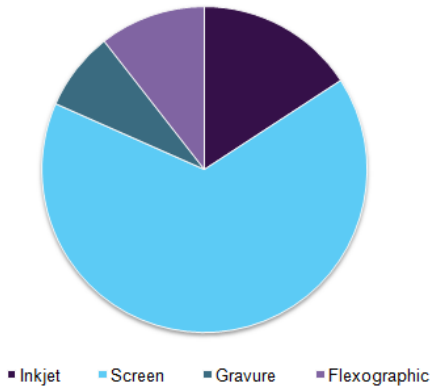

Fig. 3 Global printed electronics by printing technology (GrandViewResearch, 2017)

Recently, a new class of carbon nanoparticles which the size is less than 10 nm was discovered by Sun et al in 2006 which is the carbon dots (CDs) (Y. P. Sun et al., 2006) The CDs are also known as carbon quantum dots. These carbon nanodots are increasingly popular due to their unique optical properties, good biocompatibility, low toxicity, great aqueous stability, facile synthesis, multicolour wavelength tuned emission, up-conversion photoluminescence and high quantum yield (X. Sun & Lei, 2017), (Sharma et al., 2017), enable them to be applied in chemo- and biosensing field,

or mainly use as photoluminescence sensor which able to illuminate to detect certain compounds such as Cu^{2+}, Cr^{6+}, Ag^{+}, Au^{3+}, K^{+}, etc. (X. Sun & Lei, 2017) Despite its wide range of application, there is not many reports on the conducting properties of the individual CDs to reflect its application for electrical fields except the effort by Bhattacharjee et al. (Bhattacharjee et al., 2015). They have shown the conducting properties of poly (4-styrene sulphonate) stabilized carbon quantum dots (PSS-CQDs) and can be made into the nano-electronic switch. The individual PSS-CQDs showed metallic behaviour and able to conduct based on the interface between the composite matrix and the quantum dot (QD) surface.

Carbon dots have been widely applied in the electrochemical field, used as an enhancer on the surface of the electrode to increase the conductivity and detection towards a certain chemical. However, there is no reports that reporting on carbon dots properties as a conductive ink and its application as a screen-printed electrode. With all the desirable properties that CDs have possessed, CDs are able to take a step further in the PE industry by studying its conducting properties as conductive ink and fabricating CDs-based ink into the electrochemical sensor.

1.2 Problem Statement

Conductive ink has big potential to be discovered with more of its feature and flexibility in terms of shape, size and electrical performance. However, influence of binder in conductive ink is not well-known which needs more research to provide optimum and lowest resistance with great conductivity. Besides, different type of binder can influence the performance of casted sensor strips as an electrochemical sensor. Therefore, different type of binder will be used as a comparison to investigate its effect. Carbon dots have exhibited desired properties such as good biocompatibility, low

toxicity, great aqueous stability, water-soluble, facile and easy synthesis and its photoluminescence properties, making it as an advantage to be used as biosensor or photo-imaging. Carbon dots were used by various researchers as well for electrochemical sensor purposes by doping the carbon dots with other elements or screen-coated on glassy carbon electrode due to its conductivity and certain functional groups existed on the carbon dots surface. However, no article or journal reports on the individual characteristic of carbon dots but its pairing with other elements. Besides, due to its properties, fabricating this new carbon nanoparticle types will explore more on its conductivity as well its application in various field. Therefore, in this research, carbon dots are proposed to be used as conductive ink filler as the main conducting element and use the conductive ink to fabricate a screen-printed electrode to study its properties and effectiveness towards vitamin C detection. It seems that the properties and details of carbon dots can be further explored which may advance its usage in the printed electronics industry.

1.3 Objectives

i. To prepare conductive ink with lowest resistance by different combination and ratio of filler which is CB, binder such as PVA and PMMA and additives which is CDs.

ii. To prepare and study the properties such as resistance, conductivity, abrasion resistance, performance stability of the prepared conductive ink with different ratio of filler : binder : additives in the conductive ink formulation as an unsupported sensor strip.

iii. To study and compare the voltammetry response of pristine and CDs coated conductive ink towards the response of detecting vitamin C.

CHAPTER 2 LITERATURE REVIEW.

2.1 Properties of Carbon Dots (CDs) with their synthesis method and application

Carbon dots have many applications in various fields. From **Table 1**, its applications as a conducting material, a capacitor, a sensor, or a printing ink with their synthesis method from different precursor were clearly displayed.

The common carbon precursor for CDs synthesis is citric acid as reported by Bhattacharjee, et al. (2015a), Dang et al. (2016), Devadas et al. (2018) and Koutsioukis et al. (2019). Other carbon sources such as graphite rod or pineapple peel can be used as well.

Hydrothermal method involves the heating of carbon sources in aqueous solution above the ambient temperature and pressure for crystal growth. The hydrothermal method is commonly used to produce CDs. All the hydrothermal method carried out by mixing the carbon source with a solvent and autoclave at high-temperature range from 150 – 230 °C for about 2 – 5 h. Another two different methods were adopted by Bhattacharjee et al. and Zhuang et al. (Bhattacharjee et al., 2015a; Z. Zhuang et al., 2016). Bhattacharjee et al. dissolved the citric acid in water before pyrolysis in furnace at 200 °C for 2 h. The difference between these two methods is that the hydrothermal method heats the mixture in liquid form, while pyrolysis heats the mixture in dry form. Zhuang et al. and Tan et al. (Tan et al., 2017; Z. Zhuang et al., 2016) reported a redox reaction was used to produce the CDs. The carbon act as the working electrode and counter electrode in a supporting electrolyte, water or NaOH. Constant voltage or cyclic potential can be applied. As the oxidation time increase, the colour of electrolyte changed from colourless to light yellow or black indicated the formation of CD. Purification is required in all the work after the main reaction of

Table 1 Comparison of CDs synthesised from different method with respective properties and applications

Carbon Source	Method of synthesis	Properties	Application	Reference
Citric acid	Evaporation in Milli-Q water, followed by pyrolysis in furnace at 200 °C for 2 hours. Dialysis for purification.	Size: 5±2 nm	Conducting materials	(Bhattacharjee et al., 2015b)
Citric acid	Hydrothermal by autoclaved at 180 °C for 5 hours. Dialysis and freeze drying for purification.	Size: 3 – 5 nm Amino groups present on surface	Supercapacitors	(Dang et al., 2016)
Citric acid	Hydrothermal by autoclaved at 230 °C for 4 hours.	Size: 5 nm Carboxylic groups present on surface	Capacitors	(Devadas & Imae, 2018)
Citric acid	Hydrothermal by autoclaved 150 °C for 4 hours. Solid phase extraction and dialysis for purification.	Size: 2-2.5 nm	Gravure Printing	(Koutsiouki s et al., 2019)
Pineapple peel	Hydrothermal by autoclaved at 150 °C for 2 hours. Extraction, dialysis and centrifugation for purification.	Size: 2 – 3 nm Hydroxyl group present on surface	Sensor, molecular keypad lock and memory devices	(Vandarkuzhali et al., 2018)
Graphite rod	Graphite rod as working electrode while NaOH as electrolyte, potential applied till formation of CDs. Centrifugation and dialysis for purification	Size: 3 – 4 nm Hydroxyl, carboxylic and carbonyl group on surface of CDs	Modified electrochemical sensor	(Z. Zhuang et al., 2016)
Carbon rod	Two carbon rods used as anode and cathode in water. Constant voltage applied and stirred until the formation of CDs. Quantitative filtering and centrifugation for purification	Size: 1 – 7 nm	Modified electrochemical sensor	(Tan et al., 2017)

synthesis to remove impurities or solvent on the CDs. Purification such as dialysis, centrifugation, solid-phase extraction or quantitative filtering can be used.

Comparing at the size of CDs produced by different methods, the direct effects of synthesis methods are insignificant. The particle size ranged from 2 – 5 nm was produced by the hydrothermal reaction while the particle size of 1 – 7 nm was produced in the redox reaction. The particle size variation could be induced by the temperature or duration differences in the synthesis. However, all the CDs produced were still below 10 nm.

Through the application of CDs in conducting materials, capacitors, sensor, and electrochemical modified sensor, CDs exhibited excellent electrical conductivity. The electrical conductivity of individual CDs was investigated by Bhattacharjee et al. (Bhattacharjee et al., 2015a), stating that the CDs are natural conductors. This attribute to the carbon-carbon sp^2 hybridization, allowing the overlapping of π bond of adjacent carbon atoms together with poly(4-styrene-sulphote) that doped on the CD for stabilization of surface site. This was further supported by Pal et al. (Pal et al., 2016) where the conductivity of CDs attributed to the presence of sp^2 C-C bonds, allowing conjugation of the adjacent π- and π*- bands. The hybridization of the sp^2 are shown in **Fig. 4** where hybridized orbital will form σ bond with adjacent compounds while the leftover *p* orbital will exist as π bond. Therefore, the interface between the composite matrix and CDs surface is important to determine the conductivity of the composite. As the CDs were coated on the glass surface, high current of 1.5 nA was detected at particle site and 0.4 nA was detected at the background; Both work of Dang et al. (Dang et al., 2016) and Devadas et al. (Devadas & Imae, 2018), CDs could enhance electrical conductivity and capacitance. Dang et al. showed that CDs reduced the agglomeration of graphene sheets when doping with reduced graphene oxide (rGO), increasing the

specific capacitance of rGO up to 211.9 F/g at current density of 0.5 A/g which could be considered as supercapacitors. The amino groups on the CDs surface played an important role in the interaction with rGO. The excessive amino group could cause the CDs particle to be wrapped by rGO sheet, decreasing the surface area. Devadas et al (Devadas & Imae, 2018) showed that CDs were able to act as a junction between the polymer network; and to improve electron transfer. However, excessive CDs would reduce the capacitance of conducting polymer composite. This is because the high number of less-conductive CDs (compared to polymer) inhibited the conductivity and reduced surface area of polymer.

Tan et al. (2017) and Zhuang et al. (2016) reported the use of CDs to modify the carbon electrode as the electrochemical sensor. The deposition of CDs enhanced the electron-transfer kinetics and the current intensity of pristine electrode. The carbonyl group in CDs/electrode promoted detection of ferric ions by improving the interaction with the ferric ion and forming complexes that increased electrical conductivity by 734%. The CDs and gold (Au) nanoparticle doped on glassy carbon electrode for nitride detection showed a similar result, with the functional group on CDs surface for Au nanoparticle to anchor, nucleation and growth. Therefore, the functional group on the CDs surface is important as they react with either the other doping materials, substrate or even the detecting chemical for improving result through the creation of a higher electrical conductivity. Thus, CDs possess high potential as the filler for conductive ink.

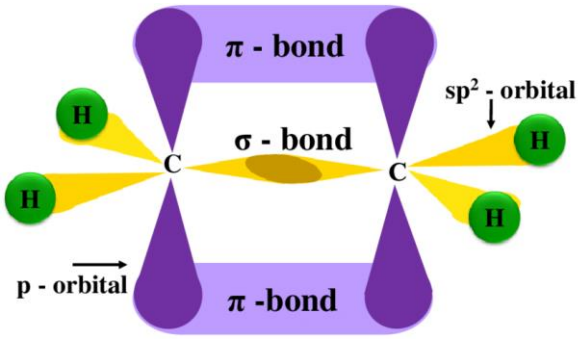

Fig. 4 The hybridization of sp2 of carbon-carbon bonds which result in σ bond formation in C_2H_4 (Iordania Constantinou, 2016)

2.2 Application of different conductive ink in electrochemical sensor

Table 2 showed different type of conductive ink that was utilised as an electrochemical sensor with the necessary parameter required when carried out the experiment. Different substrate and printing techniques were utilised to produce the sensor. Variety of electroactive area, resistivity charge, linear range and limit of detection and recovery was observed with different type of conductive filler.

The conductive ink blended with different fillers was used in electrochemical detection of desired components. There are many types of carbon nanoparticles such as carbon nanotube, graphite, graphene, carbon dot, graphene oxide, etc. Carbon-based conductive ink (**Table 2**) was blended with graphite powder and graphene nanosheet as filler; for the electrochemical sensing. Graphene is a monoatomic layer of graphite while graphite is made up of many layers of graphene. A binder ensures the conductive fillers can be connected to each other and offer good formability during printing with consistent viscosity. (Favaro et al., 2005) The common binder used are glass varnish, xantham gum and polyvinyl acetate and nail polish. The nail polish is mainly composed of plasticizers, organic solvents, nitrocellulose and thixotropic agents. Plasticizers are able to assist the film to be; flexible, durable with high resistance. The organic solvent stabilizes conductive ink, while nitrocellulose allows the formation of thin films, and

Table 2 Type of conductive ink used as electrochemical sensor and parameter involved

Type	Conductive Ink Filler and binder	Filler Percentage (%)	Substrate	Printing Technique	Electroactive area (cm2)	Resistivity (Charge transfer)	Chemical of Detection	Linear range/LOD (µmol/L)	Recovery (%)	Reference
Carbon-based	Graphite powder and nail polish	80	Paper	Handwritten with paint brush	0.189	-	Dopamine	30 – 100 / 5.2	-	(Araújo et al., 2020b)
	Graphite powder and nail polish (MWCNTs as additive)	52	Plastic	Screen-printing	0.714 – 0.822	29 Ω	Caffeic acid	2 – 5 / 0.2	99 – 109	(de Araujo Andreotti et al., 2019)
	Graphite powder and nail polish	52	PET	Screen-printing	0.45	13.6 kΩ	Hydroquinone Epinephrine serotonin	5 – 100 / 0.012 5 – 100 / 0.31 1 – 50 / 0.1	88.8-107	(Pradela-Filho et al., 2020)
	Graphite powder and glass varnish	50	PET	Screen-printing	0.186	39 kΩ	Dopamine Catechol Hydroquinone	15-100 / 4.1 10-1000 / 9.0 10-1000 / 5.3	85 – 95	(Jiang et al., 2018)
	Graphene nanosheet and Xantham Gum	98.7	PET	Handwritten with brush	-	131±10.8 Ω	Cadmium Ion	1 – 3162.27 / 0.316	98.13	(Mohanraj et al., 2020)
	Graphene nanosheet and polyvinyl acetate	~99	Paper	Handwritten with brush	85.625 m2/g	-	dsDNA	0.2 – 5 pg/mL / 0.68pg/mL	-	(Jadav et al., 2018)

Table 2 Type of conductive ink used as electrochemical sensor and parameter involved (Continue)

Type	Conductive Ink Filler and binder	Filler Percentage (%)	Substrate	Printing Technique	Electroactive area (cm2)	Resistivity (Charge transfer)	Chemical of Detection	Linear range/LOD (µmol/L)	Recovery (%)	Reference
Metal-based	Silver nanoparticle and with thermoset epoxy	90-94	Polyester	Screen-printing	-	1.3-38.4 Ω	Vitamin C	283.89 – 3406.69 / 200	92.1 – 106.84	(Kant et al., 2020)
	Silver nanoparticle with polyvinyl pyrrolidone	50	Paper	Inkjet printing	-	41 mΩ.cm	Nitrate Ion	60 – 1000 / -	-	(Na et al., 2019)
	Copper nanowires and ethyl cellulose with ethylene glycol butyl ether (solvent)	50	Glass	Screen-printing	0.0147	35 mΩ.cm	Glucose	0.001-1000 / 0.001	-	(Bardpho et al., 2016)
Composite	Graphene and PANI composite	39.3	PET	Screen-printing and Inkjet Printing	-	-	Gallic acid Epigallocatechin Catechin Caffeic acid	0.1-10/1.38 0.01-10/1.8 0.01-10/1.94 0.01-10/1.93	89.3 – 110	(X. Wang et al., 2018a)

thixotropic agents maintained the viscosity of the ink formulation. (Jadav et al., 2018) The conductive ink with viscous formulation is important to prevent the shape deformation of the electrode. The viscosity of range 1500 – 4500 cP is ideal for screen printing (X. Wang et al., 2018a). Two types of substrate mainly used which were papers and plastics such as polyethylene terephthalate (PET) and polyester. Paper is used due to its environmental-friendly properties and suitability for making disposable or single-use sensor, PET is chemical inertia with the good barrier to humidity and gases. Therefore, the substrate selection depends on the sensing purpose and the adhesiveness of conductive on the substrate. Screen printing, inkjet printing or application by hand are normally used but application by hand may create an inconsistent shape for the electrode produce with different force applied.

The conductive ink blended with different fillers was used in electrochemical detection of desired components. There are many types of carbon nanoparticles such as carbon nanotube, graphite, graphene, carbon dot, graphene oxide, etc. Carbon-based conductive ink (Table 2.2) was blended with graphite powder and graphene nanosheet as filler; for the electrochemical sensing. Graphene is a monoatomic layer of graphite while graphite is made up of many layers of graphene. A binder ensures the conductive fillers can be connected to each other and offer good formability during printing with consistent viscosity (Favaro et al., 2005). The common binder used are glass varnish, xantham gum and polyvinyl acetate and nail polish. The nail polish is mainly composed of plasticizers, organic solvents, nitrocellulose and thixotropic agents. Plasticizers are able to assist the film to be; flexible, durable with high resistance. The organic solvent stabilizes conductive ink, while nitrocellulose allows the formation of thin films, and thixotropic agents maintained the viscosity of the ink formulation (Jadav et al., 2018). The conductive ink with viscous formulation is important to prevent the shape

deformation of the electrode. The viscosity of range 1500 – 4500 cP is ideal for screen printing (Araújo et al., 2020b). Two types of substrate mainly used which were papers and plastics such as polyethylene terephthalate (PET) and polyester. Paper is used due to its environmental-friendly properties and suitability for making disposable or single-use sensor, PET is chemical inertia with the good barrier to humidity and gases. Therefore, the substrate selection depends on the sensing purpose and the adhesiveness of conductive on the substrate. Screen printing, inkjet printing or application by hand are normally used but application by hand may create an inconsistent shape for the electrode produce with different force applied.

The electrochemical area is calculated are based on the size of electrode produced, most are within the range of 1 cm^2. However, the electrode produced by Araújo et al. (2020) are having the highest electroactive area of 0.714 to 0.822 cm^2 and the lowest charge transfer resistance of 29 Ω. This is because additional multi-walled carbon nanotubes (MWCNTs) were added on the electrode surface for facilitating the charge transfer. The other carbon-based electrode produce is having high resistance charge transfer up to 39 kΩ. The low charge transfer was due to the porous surface of ink on the sensor, with no full coverage, lowering down the electroactive area (Zhu & Zhao, 2019). The resistance of carbon-based material is considerably high. However, to decrease the resistance, the electrochemical area can be increased. The electrochemical area determines the amount of reaction site, which determines the rate of chemical reaction on the electrode surface which is charge transfer in this case. (Na et al., 2019) Therefore, the higher the electroactive area, the lower the resistance possesses. The linear range is the detection range that the sensor can work on with limit of detection (LOD) which is the limit of amount of the chemical that can be detected. The lower the LOD with a wider range of linear range, the better the sensor. However, it still depends

the sensor selectivity towards the desired chemical, which in turn determine the recovery percentage. The more accurate of recovery percentage, the more precise of the sensor. According to AOAC Official Methods of Analysis Guidelines for Standard Method Performance Requirements, recovery percentage ranging from 80 – 110 % are satisfactory when concentrations of analyte in range of 1 – 10 ppm. Looking at all the recovery percentage obtained by these electrodes, they were considered as good as a sensor.

Metal conductive ink is using metal nanoparticle as the conductive ink filler such as silver, copper and even gold. These metal nanoparticles are used due to their high conductivity, however, the higher cost compared to carbon-based. Similar to carbon-based conductive ink, various type of substrate and printing technique can be used. To determine the viscosity of metal nanoparticle, solvent such as ethanol or ethylene glycol butyl ether are needed. In the study reported by Na et al. (Na et al., 2019), the electroactive area of a single copper nanowire is 0.0147 cm^2. Due to its nature of high conductivity, the resistance is much lower compared to carbon-based, similar to other metal conductive ink as well. The detection for glucose in the study conducted by Na et al. (2016) was in a great performance with extremely low LOD and large linear range.

Composite conductive ink is a combination of mixing at least two of either conducting polymer, carbon nanoparticle or metal nanoparticle in the ink. These reports (Bonet-San-Emeterio et al., 2020; Hu et al., 2014; Li et al., 2015; Tan et al., 2017; Z. Zhuang et al., 2016) have mixed graphene and polyaniline nanocomposite (PANI) as the conductive ink and cast it on a carbon-based SPE which was casted on PET. The current flow in the electrode could be increased by adding number of layers printed on the electrode, but decreased when too much was casted due to graphene aggregation

and surface area reduction. It was demonstrated that G/PANI was able to increase the surface area of pristine SPE and improve the electrochemical sensitivity, lowering the linear range of detection. Satisfactory recovery percentage was obtained by measuring samples.

Therefore, carbon-based conductive ink is generally having higher charge transfer resistance compared to metal fillers. However, the resistance can be lower with higher electroactive area by casting optimum amount of conductive ink on the substrate, prevent the agglomeration of nanoparticles. Even though the resistance is higher, the cost of carbon-based are far cheaper than other choices, which is good selection for disposable and single-use sensor. In the preparation of carbon dots conductive ink, a binder is required to reach a certain consistency and viscosity to ensure good coverage of on the substrate, besides having adequate concentration of CDs for electrical conductivity purposes with maximum electroactive area and low resistance.

2.3 Performance of Carbon Dots (CDs) modified electrode for electrochemical sensor

CDs were used as the modifier for commercial electrode. As summarized in **Table 3**, CDs were added to the surface of either glassy electrode, carbon electrode, or SPE that are already produced and available. As CDs were added on the surface of the bare electrode (Tan et al., 2017), the enhancement of current in the range of 46.47% to 734% was reported. The variation could be due to difference in CDs, as well as the detection of chemical with other conditions. CDs were proven to have great electrical conductivity properties for the improvement of the electron transfer (Z. Zhuang et al., 2016). Besides, the addition of CDs provides more conductive electrode surface (Tan et al., 2017)

Table 3 Performance comparison of CDs modified electrode

Materials	Current Increment compared to bare electrode	Chemical of Detection	Linear range/LOD (µmol/L)	Recovery (%)	Mechanism	References
CDs	734%	Ferric Ions	0.5 – 25 ppm / 0.44	92.34 – 97.45	-	(Z. Zhuang et al., 2016)
CDs/Gold nanohybrids	27.27%	Nitrite Ion	0.1 – 2000 / 0.06	92.2 – 100.7	-	(X. Zhuang et al., 2016)
CDs/Graphene	728% 131.4 – 400.8% (CDs only)	Dopamine	0.1 – 600 / 0.03	99.1 – 100.7	Diffusion	(Li et al., 2015)
CDs	220%	Dopamine	0.15 – 150 / 0.026	98.5 – 102.7	Adsorption	(Li Liu et al., 2019)
Fluorine/Nitrogen /CDs/laccase	211%	Catechol	12 – 450 / 0.014	108 - 137	Diffusion	(Fu et al., 2018)
Nitrogen/CDs	50%	Paracetamol Hydrogen Peroxide	0.5 – 600 / 0.157 0.05 – 2250 / 0.041	95.07 – 98.56	Adsorption	(Bonet-San-Emeterio et al., 2020)
CDs **Nitrogen/CDs** **Sulphur/CDs**	46.67% 40% 25%	Salicylic Acid	- / 101 - / 91.2 - / 94.8	-	-	(Ji et al., 2016)

Table 3 (Continue)

Materials	Current Increment compared to bare electrode	Chemical of Detection	Linear range/LOD (µmol/L)	Recovery (%)	Mechanism	References
Nitrogen/CDs	9%	Glucose	1000 – 12000 / 250	-	Adsorption	(Hu et al., 2014)
CDs	47.7%	Dopamine	- / 0.0015	99 – 110.8	Diffusion	(Wei et al., 2014)
rGO/CDs	213.3%					
Nafion/MWCNT/ CDs/MWCNT	400%	Hydroquinone Catechol Resorcinol	1 – 200 / 0.07 4 – 200 / 0.06 3 – 400 / 0.15	100.3 – 109.8 96 – 105.8 83.4 – 101.6	Diffusion	(Z. Zhuang et al., 2016)

*rGO = Reduced Graphene Oxide

Different chemicals were added into CDs to form nanohybrids which could enhance the overall electrical conductivity namely nitrogen, fluorine, sulphur, MWCNTs, graphene or gold. These components will attach to the functional groups on CDs, and the resulted nanohybrids can enhance the detection of chemicals. As mentioned in Section 2.1, it was found that the functional groups on the surface of CDs act as an anchor site for the attachment of gold nanoparticle. Besides, the CDs act as a reductant and stabilizer for the synthesis of gold nanoparticle on the surface (X. Zhuang et al., 2016). The sensitivity of the modified electrode towards dopamine was increased with the addition of CDs through electrostatic interactions. This is due to the negative charge carbonyl group on the surface of CDs, which able to attract cationic dopamine to the electrode while preventing anionic substances to be detected (Li et al., 2015). The similar result yielded in the studies by Li Liu et al. (Li Liu et al., 2019) and Hu et al (Hu et al., 2014). The selectivity towards dopamine was enhanced due to electrostatic interactions, while preventing anionic ascorbic and uric acid from being detected even though with 100 folds of concentration than dopamine.

In the research conducted by Liu et al. (Fu et al., 2018), the fluorine, nitrogen-doped CDs (F,N-CDs) were added as a bridge for accelerating electron transfer process while facilitating the oxidization of catechol to o-benzodiquinone. The hypothesis was further supported by the work reported by Fu et al. (Ji et al., 2016) which proved the functional groups present on the N-CDs acted as regulators, with the oxygen-containing groups withdrew 2 protons from endiol groups to facilitate paracetamol oxidation. With the oxidation occurred, the current flow was detected by the sensor. In the detecting of hydrogen peroxide, the N-CDs increased the adsorption energy for more adsorption of hydrogen peroxide to the electrode. Ji et al. (Bonet-San-Emeterio et al., 2020) showed that the NCDs could switch the monoatomic end-on adsorption of pristine CDs to

diatomic side-on adsorption, which effectively weakens the O-O bonding for oxygen reduction. Therefore, nitrogen doping induced charge delocalization in CDs, accelerated electrocatalysis, and switched the mechanism of redox reaction to a more effective one. However, Bonet-San-Emeterio et al. (Wei et al., 2014) mentioned that the oxidation potential decreased slightly due to the presence of amine and amide groups in N-CDs. These functional groups reduced the electro-donor character of doped N and S-CDs. In order to increase or produce the electroactive area, surface activation is required by creating new oxygenated groups or create porous in the ink surface in non-conductive organic compounds. In the Nafion/MWCNTs/CD/MWCNT composite, the MWCNT increased the surface area for efficient electron transfer and porous structure for the oxidation of hydroquinone, catechol and resorcinol (X. Zhuang et al., 2016).

The mass transfer mechanism is another important parameter that affects the oxidation and reduction process on the electrode surface, either adsorption or diffusion-controlled. When the scan rate is increased, the redox peak current increases correspondingly with cathodic and anodic peak against the square root of scan rates, showing that the electro-redox is a diffusion-controlled process (Fu et al., 2018). If the peak current is linearly proportional to the scan rate, then it involves adsorption-controlled mechanism (Fu et al., 2018). Another method would be by plotting graph of logarithm scan rate against logarithm current, with the slope equals to 0.5 indicating diffusion-controlled mechanism and slope equals to 1 indicating adsorption-controlled mechanism. The chemicals diffuse into the subsurface below the interface from the bulk solution during diffusion while the chemicals only reach at the interface of bulk solution during adsorption. Both kinetic shows that the potential applied on the electrode can increase or decrease the rate of oxidation and reduction.

From **Table 3**, all the linear range, LOD and recovery percentage are in the acceptable range. However, F/N-CDs/laccase and rGO/CDs sensors attained a recovery percentage of 137% and 110.8%, respectively. When the recovery percentage exceeded the standard range of 80% – 110%, the sensor couldn't be used effectively. Other important parameters that affect the efficiency of the electrochemical sensor are selectivity, reproducibility and stability. The selectivity test is frequently conducted by adding chemicals that have similar properties of the desired chemical of detection in the same solution. Then the detection is tested to see if any interference towards the response when the concentration of the similar chemicals increases. As discussed earlier, certain functional group on the surface of CDs can increase specificity based on electrostatic interaction. Reproducibility refers to the ability of the sensor to produce a similar result with the same concentration of chemicals. The lower the relative standard deviation (RSD) between the result produced causes higher reproducibility. The RSD produced when sensing the paracetamol and hydrogen peroxide was about 3.2% and 3.7% respectively, such RSD indicates great reproducibility as reported (Ji et al., 2016). High reproducibility was reported by Ji et al (Z. Zhuang et al., 2016), where the RSD for glucose detection was only 1.04%. Stability refers to the ability to maintain the performance of the sensor after produced several days or after testing for many times by observing its current performance or observe the RSD result. The sensitivity dropped to 89% showing the stability of the CDs/Gold electrode after 20 days (Li Liu et al., 2019). Great stability was shown as well when the current only dropped 0.57% after 50 times of testing with cyclic voltammetry (Jeney-Nagymate & Fodor, 2008). For the detection of paracetamol and hydrogen peroxide, the current signals decreased by 5.7% and 6.2% respectively after 3 weeks and multiple sensing, indicating the sensor was stable to be used for many times.

Therefore, CDs are a good electrical conductor as they were used as a modifier for the electrode in electrochemical sensing applications. The functional groups that may present on the surface depending on the synthesis method. The functional groups help to characterize the electrode produced, enable better doping with other chemicals or provide higher selectivity to the desired chemicals. However, the electrode produced must able to yield a recovery range of 80 – 110%, with a wide range of linear range and low LOD for the best efficiency. With a high selectivity, stability and reproducibility, a good and sensitive sensor can be commercialized for standard usage.

CHAPTER 3 METHODOLOGY

Fig. 5 shows the activity of the research.

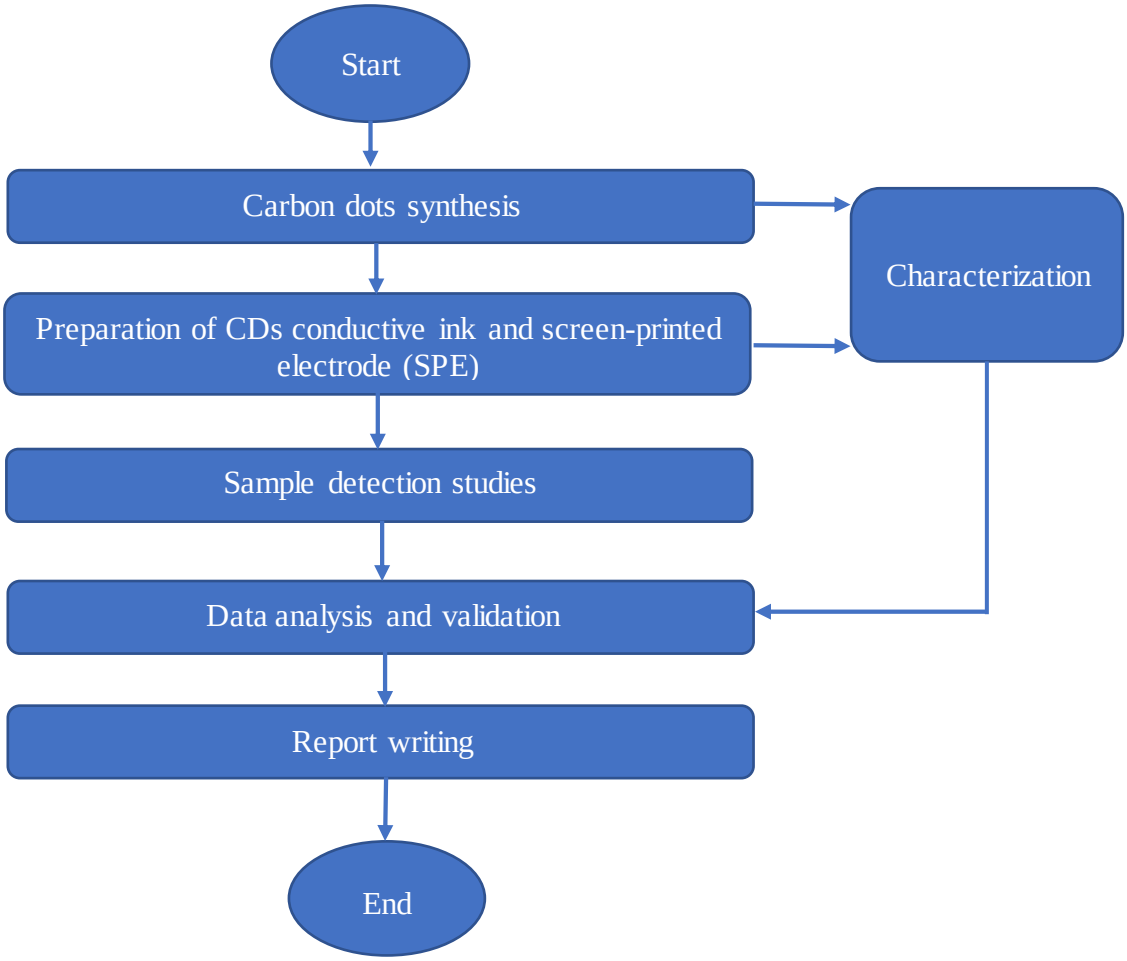

Fig. 5 Flow diagram of research project on CDs conductive ink and screen-printed electrode