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# Ultra-high performance liquid chromatographic determination of antioxidants in teas using inkjet-printed graphene–polyaniline electrode <sup>☆</sup>



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## ABSTRACT

A development of ultra-high performance liquid chromatographic coupled with a novel inkjet-printed conductive ink-modified electrode for a fast and simultaneous determination of polyphenolic antioxidants was achieved. Two printing techniques were selected for fabrication and modification including (i) an in-house screen-printing method and (ii) an inkjet-printing method, respectively. A conductive ink containing graphene and polyaniline nanocomposite (G–PANI) was precisely casted onto the surface of screen-printed carbon electrode (SPCE) using a dimatix inkjet material printer. Compared to a bare SPCE, the G–PANI-modified screen-printed carbon electrode (G–PANI/SPCE) exhibited higher electrochemical sensitivity with increase (2–4 times) of peak current of each antioxidant. Moreover, four antioxidants were successfully separated and determined within 3 min using a reverse phase ultra-high performance liquid chromatography (UHPLC) with a mobile phase containing phosphate buffer and acetonitrile (90:10 v/v). Under an optimal detection potential at +1.2 V vs. Ag/AgCl, linear calibrations and limits of detection ( $S/N=3$ ) for antioxidants were found to be 0.01–10  $\mu\text{g mL}^{-1}$  and 1.38–1.94  $\text{ng mL}^{-1}$ , respectively. Finally, this proposed method has been successfully used for the determination of antioxidants in tea samples, the results obtained from our presented method were within a highly good agreement those obtained from a standard UHPLC–UV method.

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## 1. Introduction

Tea is one of the most widely consumed beverages in the world. A commercial dried tea has been normally collected from tea leaves which a scientific name is *Camellia sinensis* from an Aceae family of the Theales order [1,2]. Tea consumption has linked with decreased risks including cancer, cardiovascular abnormalities, arthritis, and pathogenic infections [3]. A tea infusion provides numerous essential compounds for a human health such as polyphenolic antioxidants, caffeine, amino acids, vitamins, carbohydrates, and trace elements [4]. The conventional tea beverage contains a variety of major polyphenols

consisting of epicatechin (EC), epicatechin-3-gallate (ECG), epigallocatechin (EGC), epigallocatechin-3-gallate (EGCG), catechin (C), gallic acid (GA), and caffeic acid (CFA). To monitor a quality control of tea, a determination of these polyphenol contents in the tea as well as in the beverages is very important in the various research fields including nutritional and epidemiological studies. Therefore, it is necessary to develop an appropriate approach to determine the phenolic compounds simultaneously in tea samples to evaluate their qualities and health promoting properties.

Various conventional analytical methods for separation and simultaneous determination of polyphenolic antioxidants have been reported [5–7]. One of the remarkable technique to measure these antioxidants is high performance liquid chromatography (HPLC). However, the HPLC method provided the limitation in term of time-consuming which all separation and determination processes were longer than 30 min approximately [8,9]. To decrease the separation time for simultaneous measurement of polyphenolic antioxidants, ultra-high performance liquid chromatography (UHPLC) has become an interesting technique to produce high-throughput analysis

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because of its fast analysis and high resolution [10,11]. For detection mode, an electrochemical detection offers high potential of interest. They can be used as a detector in the UHPLC system for the determination of varietal electroactive antioxidants [12–14]. Various electrode materials have been also applied to detect these electroactive polyphenolic compounds such as metal electrode (platinum electrode [15]), glassy carbon electrode (GCE) [16,17], carbon-paste electrode (CPE) [18] and screen-printed carbon electrode (SPCE) [19]. Among these electrode materials, SPCEs have been paid much interest due to its significantly low cost, disposability, and easy to couple with a thin-layer flow cell for the electrochemical detector in the flow-based system.

To enhance the electrochemical sensitivity of working electrode, the electrode modification has been a remarkable issue for current ongoing research. Several modification techniques have been applied such as simple drop-casting [20], electropolymerization [21,22], spin-coating [23,24], electrospraying [25] and electrospinning [26]. An inkjet printing has been demonstrated to be an attractive method for the electrode modification providing low cost, high production speed, selectivity, and compatibility with a wide range of materials and substrates. This technique is able to precisely deposit very small droplets of modifier in a picoliter level (2–12 pL) to prepare ultra-thin film onto the surface of substrate with a high production speed and a high pattern resolution [27–33]. For another strategy to improve the electrode surface area in the electrochemical system, an electrode modification using a noticeable nanomaterial has played an important role to enhance the electrochemical sensitivity of the sensors. Various kinds of nanomaterials have been used as an electrode modifier such as metallic nanoparticles (i.e. gold, silver, and platinum) [34], carbon-based nanoparticles (i.e. fullerene, single-wall carbon nanotube and multi-wall carbon nanotube) [35].

Currently, graphene (G) is a distinguished nanomaterial modifier which is highly useful for electroanalysis due to its very large two-dimensional electrical conductivity, and excellent electron transfer rate. However, the drawback of using G to modify electrode is agglomeration; therefore, to prevent this limitation of G, polyaniline (PANI) has been also used as an electrode modifier to improve the G distribution on the electrode surface. PANI is a versatile conducting polymer owing to its high electrical conductivity, thermal and chemical stability, simplicity to synthesize, and wide range of potential applications [36,37].

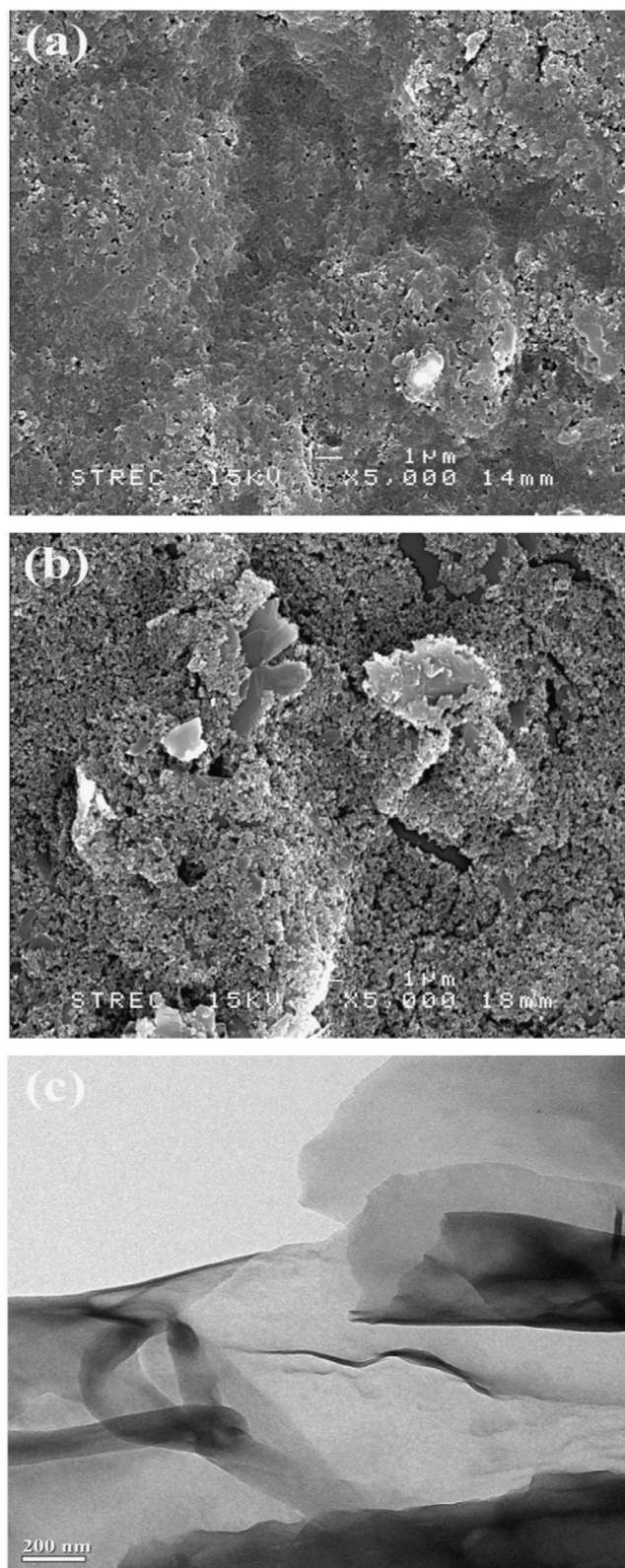
Such the benefits of G and PANI, in this work, we interested in the use of the inkjet printing technology to print the conductive G–PANI ink onto the SPCE. They would be an alternative way to enhance the electrochemical sensing and catalytic capabilities of the electrochemical detection in the UHPLC system.

Therefore, the aim of this work is to develop an outstanding inkjet-printed G–PANI-modified SPCE (G–PANI/SPCE) to use as a new electrochemical sensor for chromatographic determination of antioxidants in tea samples. The inkjet printing technology was applied to produce thin-film of G–PANI among on the surface of SPCE with high reproducibility. The physical and electrochemical properties of G–PANI/SPCE were then characterized. The optimal G–PANI/SPCE was coupled with the UHPLC system for amperometric and simultaneous determination of four antioxidants in teas.

## 2. Experimental

### 2.1. Reagents

HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Graphene (G) was ordered from A.C. S (Medford, USA). Gallic acid (GA), (–)-epigallocatechin (EGC), (+)-catechin (C), caffeic acid (CFA), ortho-phosphoric acid 85%,



**Fig. 1.** SEM images of (a) bare SPCE and (b) inkjet-printed G–PANI/SPCE prepared by inkjet printing and (c) TEM image of G–PANI.

potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), polyaniline, camphor-10-sulfonic acid ( $\text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$ ) and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich (St. Louis, USA). Milli-Q water from Milipore ( $R \geq 18.2 \text{ M } \Omega \text{ cm}^{-1}$ ) was used to prepare buffers and stock standard solutions. Stock standard solutions of GA, EGC,

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