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# Electrochemical method for detection of aspartame in beverage using Pd modified single walled carbon nanotubes sensor (PdNPs/SWCNTs)

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This study revealed synthesis and application of Pd nanoparticles (PdNPs) on single walled carbon nanotubes (SWCNTs) as aspartame sensors in beverage samples through the electrochemical analyses. SWCNTs were synthesized by chemical vapor deposition method and then Pd NPs covered on the carboxylated SWNT walls. SEM and XRD studies were used to characterize the morphology and crystalline structure of prepared films which exhibited Pd NPs that have been randomly decorated on the CNT sheets. Electrochemical characterization of PdNPs/SWCNTs as aspartame sensor was performed through cycle voltammetry (CV) measurements which indicated that the linear sensing range, detection limit and sensitivity were obtained 1 to 120 µM, 0.001 µM and 0.29587µA/µM, respectively. The comparison of prepared electrode performance with other reported aspartame sensing systems showed the lower obtained detection limit value on PdNPs/SWCNTs. Selectivity and interference response of prepared aspartame sensors was studied in presence of different substances in electrochemical cells. The applicability, accuracy and precision of the PdNPs/SWCNTs were also evaluated for aspartame determination in the prepared beverage as a real sample. The results showed the recovery values range was from 86.5% to 93.4% and relative standard deviations values were lower than 4.21% which illustrated acceptable accuracy and precision measurements on the PdNPs/SWCNTs.

**Keywords:** Single-walled carbon nanotubes; Pd nanoparticles; Aspartame; Beverage; Cyclic voltammetry

## 1. INTRODUCTION

Aspartame (L-alpha-aspartyl-L-phenylalanine methyl ester) as a nonnutritive sweetener is frequently used for sweetening a variety of beverages, pharmaceuticals and foods. It is an artificial low-calorie sweetener that is broken down into 40% aspartic acid as amino acids, 50% phenylalanine as the methyl ester, and 10% methanol during metabolism in the body[1, 2]. Studies showed that

consumption of artificially-sweetened soft drinks can be a common weight-management strategy, especially application of aspartame as a sugar substitute can significantly reduce in both calorie intakes and bodyweight in adults and children[3].

Moreover, several researches indicated that aspartame could have negative effects on human health. High levels of phenylalanine can be hazardous for people with phenylketonuria which is attributed to deficiency of the specific enzyme for breaking down the amino acid phenylalanine[1, 4]. Therefore, the identification and determination of aspartame level in beverages, pharmaceuticals and food samples are necessary and many researchers have been conducted on development, design and optimization of aspartame sensing techniques.

Aspartame sensing techniques conclude capillary electrophoresis, quartz crystal microbalance, high performance liquid chromatography, pyrolysis-gas chromatography/mass spectrometry, surface-enhanced Raman spectroscopy, microscopic Fourier transform infrared spectrometry, molecular absorption spectrophotometry, and electrochemical methods[5-11]. Many of these techniques are very expensive and with high levels of noise. In addition, several of them need highly skilled specialists, pretreatment process, complicated preparatory and analysis steps. Among these techniques, electrochemical methods have been conducted on cost-effective, rapid, accurate and friendly operation systems to study oxidation-reduction reactions and determination of organic and inorganic analytes in aquatic solutions [12-16]. Moreover, modification of electrode surfaces with nanocomposites, nanostructured materials and doping processes can promote the stability, sensitivity and selectivity of systems[17-21].For example, Balgobind et al.[22] synthesized a hybrid of ZnO NPs/MWCNTs for electrochemical detection of aspartame in food and beverage samples with a 96% confidence level. Medeiros et al. [23] reported a highly selective electrochemical method for the detection of aspartame in food with a boron-doped diamond electrode. Their results were similar to those obtained using high performance liquid chromatography technique with 95% confidence level. Therefore, this study conducted to synthesis PdNPs/SWCNTs and structural and electrochemical characterization for determination of aspartame in beverages.

## 2. EXPERIMENT

Chemical vapor deposition method was used to synthesis of SWCNTs [24].The mixture of 25 ml of 0.4 M $Fe(NO_3)_3 \cdot 9H_2O$ (≥96%, Hebei Yanxi Chemical Co., Ltd., China) and 4 g $Al_2O_3$ (99.99%, Zibo Aotai New Material Technology Co., Ltd., China ) was prepared as a precatalyst. The precatalyst mixture was dried at 25 °C for12 hours. The dried precatalyst transferred to the oven at 100°C for 24 hours, followed by calcination at 600°C for 2 hours to achieve red-brown precatalyst powder. For synthesis of SWNTs,0.5 g of precatalyst powder was placed in a furnace at 800°C for 2hours under blowing of 55 ml/minute of $N_2$ as a carrier gas was used to transfer 100 ml/minute of liquefied petroleum gas. After cooling the furnace, the grown SWCNTs were collected.

For preparation of the PdNPs/SWCNTs, the collected SWCNTs was purified in $H_2O_2$ (50%, Qingdao HiseaChem Co., Ltd., China) followed by ultrasonically washing and dispersing in ethanol. Then, dispersed SWCNTs was carboxylated in mixture of 0.1 M $H_2SO_4$ (96%, Shijiazhuang

Xinlongwei Chemical Co., Ltd., China) and 0.1 M $HNO_3$ (68%, Qingdao HiseaChem Co., Ltd., China) in volume ratio of 2:1 in ultrasonic bath for 5 hours followed by ultrasonically washing and dispersing in ethanol. After that, 30 ml of 2 M $Na_2PdCl_4$ (98%, Merck) solution was ultrasonically added to the carboxylated SWNTs. After 2 hours, the dispersed PdNPs/SWCNTs suspension was obtained. To obtain the PdNPs/SWCNTs film, the resulting suspension was transferred to the oven at 40°C for 8 hours.

Scanning electron microscopy (SEM, Model 35 CF microscope, JEOL, Tokyo, Japan) was used for structural and morphological studies of the prepared SWCNTs and PdNPs/SWCNTs films. X-ray diffraction (XRD, Siemens D5000 diffractometer, CuKα (λ=1.5418 Å), Siemens, Munich, Germany) analysis was conducted to study the crystal structure of SWCNTs and PdNPs/SWCNTs films. CV as electrochemical measurements were performed with an Autolab PGSTAT204 electrochemical workstation in three-electrode electrochemical cell which contained Ag/AgCl as the reference electrode, Pt as a counter electrode, and SWCNTs and PdNPs/SWCNTs as working electrode. The electrolyte for electrochemical studies was 0.1 M phosphate buffer solutions (PBS) which prepared of 0.1 M $H_3PO_4$ (≥85%, Henan Bright Commercial Co., Ltd., China) and 0.1 M $NaH_2PO_4$ (99%, Zhengzhou Yucai Phosphate Chemical Factory, China).

## 3. RESULTS AND DISCUSSION

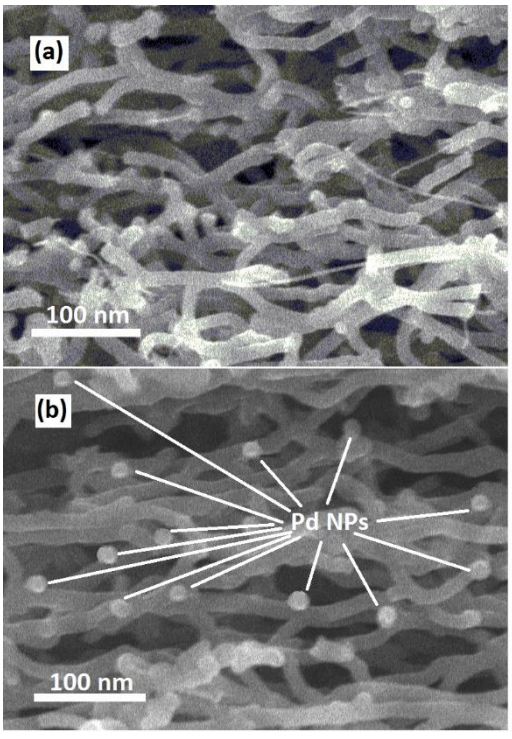


**Figure 1.** SEM images of the prepared (a) SWCNTs and (b) PdNPs/SWCNTs films.

The morphology of the prepared SWCNTs and PdNPs/SWCNTs films are shown in SEM images in Figures 1a and 1b, respectively. It can be seen that the SWCNTs film constituted by

SWCNTs networks in diameter of 30 nm. For PdNPs/SWCNTs film, SEM image displays the randomly oriented PdNPs/SWCNTs bundles which certified that Pd NPs have been decorated with CNT sheets. The spherical Pd NPs with sizes of 25 nm are covered by the carboxylated SWNT walls which indicate formation of clusters of Pd atoms.

XRD patterns of samples are exhibited in Figure 2. XRD pattern of SWCNTs shows the single diffraction peak at 25.48° that confirms the formation of the (002) plane in SWCNTs corresponding to JCPDS card No. 00-085-1638. XRD pattern of PdNPs/SWCNTs film displayed two additional peaks at 40.27° and 46.98 which were attributed to formation of (111) and (200) planes, consistent with JCPDS card No. 00 046 1043.

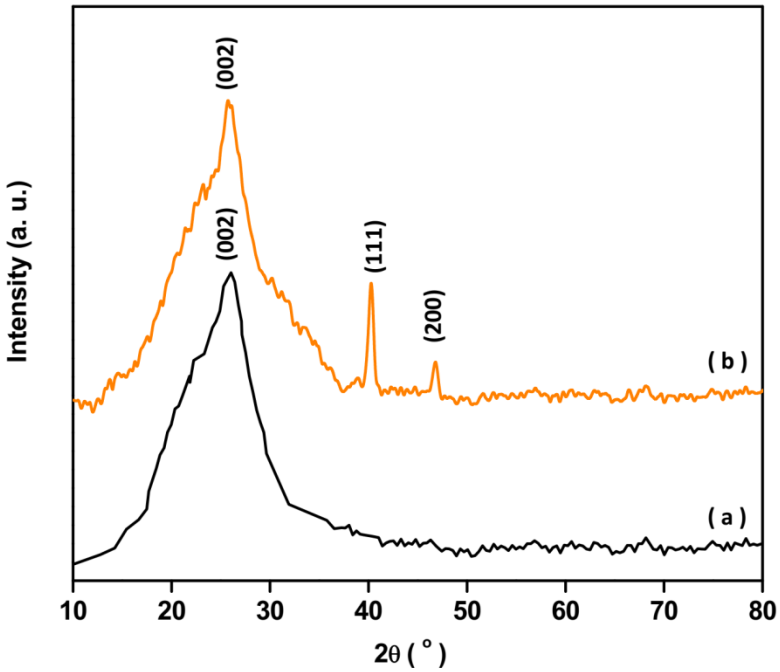


**Figure 2.** XRD patterns of the prepared (a) SWCNTs and (b) PdNPs/SWCNTs films.

Figure 3 displays the first recorded CV of SWCNTs andPdNPs/SWCNTs electrodes in potential range from -0.5V to 0.5V at 20 mV/s scan rate in 0.1M PBS (pH 7.0) containing 40 µM aspartame. It can be seen the single anodic peaks at 0.03 V for both of recorded CVs. The CV of PdNPs/SWCNTs electrodes shows sharp and higher anodic peaks current which are associated with improvement of conductivity of the electrode by anchoring of Pd NPs on SWCNTs [25]. Moreover, spherical Pd NPs can provide more active site, exposed surface area and effective electron transfer which can facilitate electrochemical reaction[26]. In order to study the stability of SWCNTs and PdNPs/SWCNTs electrode responses to presence aspartame in electrochemical, the first and 50$^{th}$ recorded CVs of both electrodes are shown in Figure 4. As observed, the anodic peak current is decreased 16.6% and 5.6% for SWCNTs and PdNPs/SWCNTs electrodes, respectively, which

demonstrated a higher stability of PdNPs/SWCNTs electrodes to presence aspartame. Therefore, following electrochemical studies are conducted on PdNPs/SWCNTs electrodes.

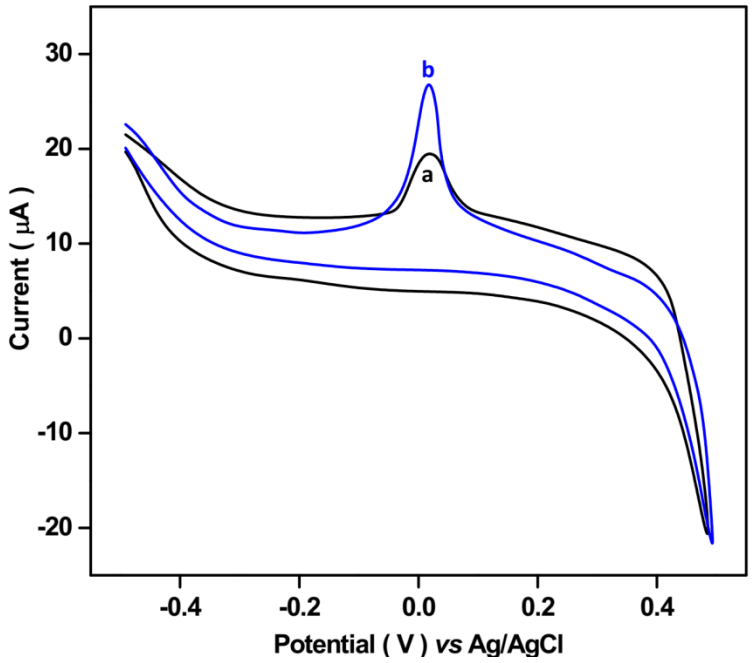


**Figure 3.** The first recorded CV of (a) SWCNTs and (b) PdNPs/SWCNTs electrodes in potential range from -0.5V to 0.5V at 20 mV/s scan rate in 0.1M PBS pH 7.0 containing 40 µM aspartame.

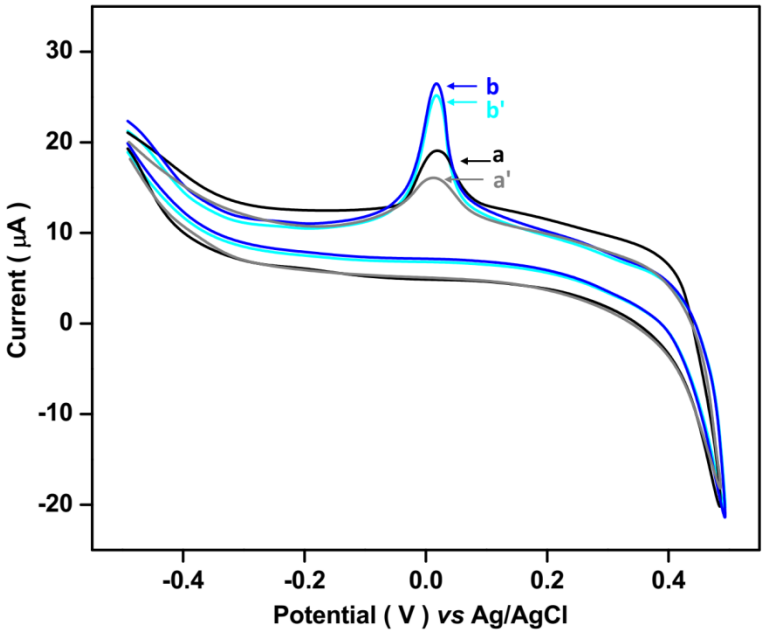


**Figure 4.** The first recorded CV of (a) SWCNTs and (b) PdNPs/SWCNTs electrodes, and 50$^{th}$ recorded CV of (a') SWCNTs and (b') PdNPs/SWCNTs electrodes in potential range from -0.5V to 0.5V at 20 mV/s scan rate in 0.1M PBS pH 7.0 containing 40 µM aspartame.

Figure 5 shows the electrochemical response and calibration plot of PdNPs/SWCNTs electrodes to various concentrations of aspartame. It can be seen from Figure 5, that the oxidation peak is linearly enhanced with increasing aspartame concentration. Thus, a broad sensing range is obtained from 1 to 120 µM. Furthermore, a detection limit and sensitivity are estimated0.001 µM and0.29587 µA/µM, respectively. The analytical performances of the reported modified nanostructured aspartame sensors are presented and compared with other aspartame sensing systemsin Table 1 which illustrated PdNPs/SWCNTs electrode suggests significant development to aspartame determination, such as improvement of the linearity ranges and limit of detection. It should be considered SWCNTs as a propitious nanostructured substrate material for providing electrodes due to uniformity, inexpensiveness, high conductivity and transparency, and favorable adherence, tensility and flexibility[25].On the other hand, Pd nanoparticles as noble metal nanostructures have shown the great potential for catalysts because of enhancement of the current response of analyte oxidation at the nonenzymatic electrode surface and enhancement of stability and reproducibility [25].

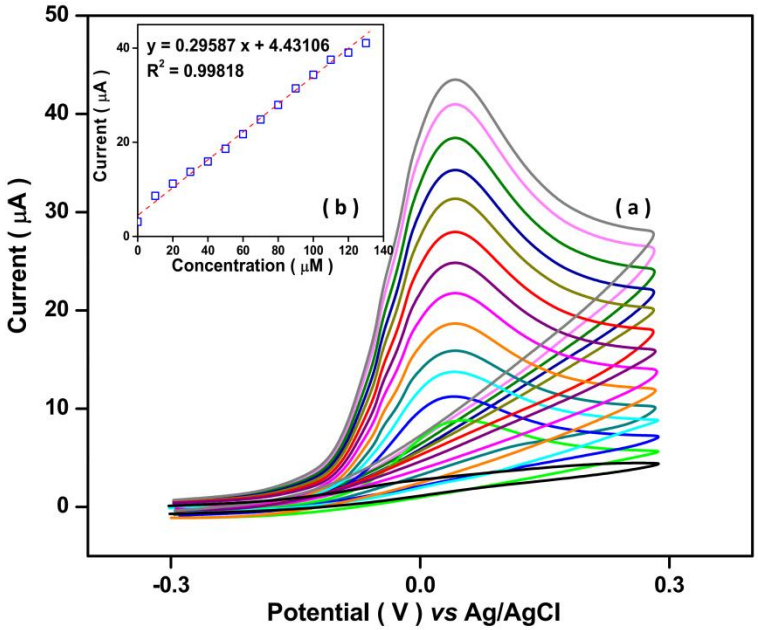


**Figure 5.** (a) Electrochemical CV response and (b) calibration plot of PdNPs/SWCNTs electrode to various concentration of aspartame in potential range from -0.3V to 0.3V at 20 mV/s scan rate in 0.1M PBS pH 7.0.

**Table 1.** Comparison between the analytical performances of the reported modified nanostructured aspartame sensors and PdNPs/SWCNTs electrode

| Electrode | Technique | Linear Range (µM) | Limit of detection (µM) | Ref. |
|---|---|---|---|---|
| Colloidal sphere-patterned polyterthiophene thin film | QCM[a] | 12.5 to 200 | 31 | [5] |

| | | | | |
|---|---|---|---|---|
| Post-column photochemical reactor | LC[b] | 3.4 to 68 | 1.7 | [6] |
| Aspartame hydrolyzing enzyme/aspartate aminotransferase/ glutamate oxidase /Immobilonmembrane | AMP[c] | 200 to 1500 | 150 | [7] |
| Preanodized screen-printed carbon electrode | DPV[d] | 0.05 to 10 | 0.0256 | [8] |
| Liquid-liquid interface | DPV | 30-350 | 30 | [27] |
| Boron-Doped Diamond Electrode | SWV[e] | 9.9 to 52 | 0.023 | [28] |
| PdNPs/SWCNTs | CV | 1 to 120 | 0.001 | This work |

[a] QCM: Quartz crystal microbalance [b] LC: liquid chromatography [c] AMP: Amperometry
[d]DPV: Differential pulse voltammetry [e]SWV: Square-wave voltammetry

Further electrochemical measurements were carried out for study of selectivity and interference response of PdNPs/SWCNTs electrodes for determination of aspartame in presence of different substances in electrochemical cells. Table 2 shows electrochemical CV response ofmodified electrode to successive additions of1 µMof aspartame and4 µMcitric acid, phosphoric acid, cyclamate, glucose, saccharin, fructose, sucrose, ascorbate, caffeine, L-phenylalanine, acesulfame-K and sodium benzoate as foreign species based on possibility of the presence in food, beverage and pharmaceutical specimens. Table 2 indicates that no analytical signal is recorded for additions of the interfering substance but after addition of the aspartame, the corresponding electrocatalytic current is recorded.

**Table 2.** The electrochemical CV response of PdNPs/SWCNTs electrode to successive additions of 1 µM of aspartame and 4 µM of interfering substance in potential range from -0.3V to 0.3V at 20 mV/s scan rate in 0.1M PBS pH 7.0

| **Interfering substance** | **Added (µM)** | **Electrocatalytic current response (µA)** | **RSD (%)** |
|---|---|---|---|
| aspartame | 1 | 0.304 | ±0.004 |
| citric acid | 4 | 0.013 | ±0.005 |
| phosphoric acid | 4 | 0.021 | ±0.008 |
| cyclamate | 4 | 0.012 | ±0.008 |
| glucose | 4 | 0.017 | ±0.007 |
| saccharin | 4 | 0.011 | ±0.009 |
| fructose | 4 | 0.013 | ±0.006 |
| sucrose | 4 | 0.010 | ±0.008 |
| ascorbate | 4 | 0.013 | ±0.003 |
| caffeine | 4 | 0.013 | ±0.004 |
| L-phenylalanine | 4 | 0.011 | ±0.009 |
| acesulfame-K | 4 | 0.021 | ±0.005 |
| sodium benzoate | 4 | 0.017 | ±0.011 |

The results is in agreement with the reports by Radulescu et al.[29] on bienzymatic aspartame biosensor through flow injection analysis, SafaeiMoghaddam et al.[30]for spectrophotometric determination of aspartame on iron porphyrinc metal–organic framework and Balgobind et al. [22] for electrochemical detection of aspartame in food and beverage samples on hybrid of ZnO NPs/MWCNTs. Therefore, the study of interference response of prepared aspartame sensors demonstrates that the interferences have not remarkably effect on the PdNPs/SWCNTs response.

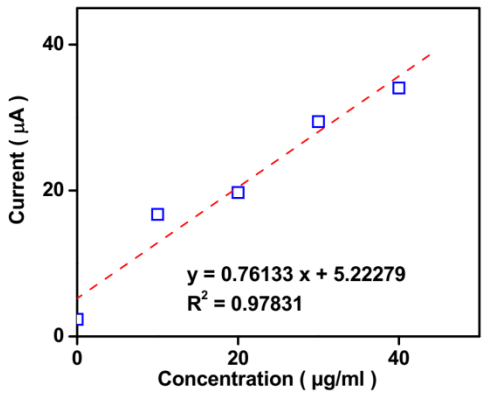


**Figure 5.** The calibration plot of electrochemical CV responses of PdNPs/SWCNTs to successive addition 10µg/ml of aspartame solutions in potential range from -0.3V to 0.3V at 20 mV/s scan rate in 0.1M PBS pH 7.0

**Table 3.** Analytical results of aspartame electrochemical detection in real samples using PdNPs/SWCNTs (n = 5)

| Real sample | Amount added (µg/ml) | Found concentrations (µg/ml) | Recovery (%) | Relative standard deviations (%) |
|---|---|---|---|---|
| beverage | 1.00 | 0.88 | 88.0 | 3.01 |
| | 2.00 | 1.73 | 86.5 | 2.11 |
| | 5.00 | 4.67 | 93.4 | 1.95 |
| | 10.00 | 9.33 | 93.3 | 4.21 |

In order to evaluate the accuracy and precision of the PdNPs/SWCNTs as electrochemical sensors for aspartame determination in prepared carbonated beverage as real sample, the concentration of aspartame in carbonated beverage sample was determined by injection prepared real sample. The carbonated beverage as a real sample was purchased from a local market and ultrasonically degassed for 15 minutes at room temperature. Then, the sample was dried and 1µg of dried powder was solved 1 ml of 0.1 PBS (pH 7.0). After then, the prepared sample was directly added with appropriate values of standard solution. Figure 6demonstrates the calibration plot of electrochemical CV responses of PdNPs/SWCNTs to successive addition 10µg/ml of aspartame solutions in potential range from -0.3V to 0.3 V at 20 mV/s scan rate in 0.1M PBS (pH 7.0). The aspartame content in the real sample is

obtained 6.86 µg/mlthat is agreed with to obtain results by Hamano et al. [31]through spectrophotometric enzymatic method. The analytical results are also shown in Table 3. These results indicates the recoveries values range is from 86.5% to 93.4% and relative standard deviations values is lower than 4.21% which demonstrated the PdNPs/SWCNTs with acceptable accuracy and precision can be used to detection of aspartame in food, beverage and pharmaceutical specimens.

## 4. CONCOUSION

This paper presented synthesis and application of PdNPs/SWCNTs as aspartame sensors in beverage samples. Chemical vapor deposition method was used to synthesis of SWCNTs and Pd NPs covered the carboxylated SWNT walls. SEM and XRD analyses were applied to morphology and crystalline structure studies of prepared films, respectively which indicated Pd NPs had been decorated the CNT sheets. Electrochemical studies of PdNPs/SWCNTs as aspartame sensors conducted on CV measurements which implied to achieve the sensing range from 1 to 120 µM, detection limit of 0.001 µM and sensitivity of 0.29587 µA/µM. The comparison of prepared electrode performance with other reported aspartame sensing systems revealed the lower obtained detection limit value on PdNPs/SWCNTs. Selectivity and interference response of prepared aspartame sensors was studied in presence of different substances in electrochemical cells. The accuracy and precision of the PdNPs/SWCNTs was also evaluated for aspartame determination in prepared carbonated beverages as real samples. The results indicates the recoveries values range was from 86.5% to 93.4% and relative standard deviations values was lower than 4.21% which demonstrated the PdNPs/SWCNTs with acceptable accuracy and precision can be used to detection of aspartame in food, beverage and pharmaceutical specimens.

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