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ORIGINAL PAPER

Electrocatalytic effect of nano-wrinkled layer carbonaceous electrode: determination of folic acid by differential pulse voltammetry

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Abstract

Nano-wrinkled layer carbonaceous electrode materials were prepared from pyrolytic carbonization of different proportions of mixtures coal tar pitch (CTP) and polystyrene (PS) composite. The PS content in carbonaceous materials was in between 10% and 70% PS. The electrodes were characterized using scanning electron microscopy (SEM) and electrochemical methods such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CTP-PS4 (50% PS content) electrode was more reductant than the other electrodes. Similarly, electrocatalytic activity of CTP-PS4 for folic acid (FA) was higher than the other electrodes. The electrode was used in the determination of FA by differential pulse voltammetry (DPV). Under optimal conditions, the anodic current of FA was linear in the concentration range from 0.25 to 40 μmol/L. The obtained linear range calibration plot of the concentration of FA vs. peak current resulted in two linear slope values. The first equation for FA was Ip(FA) = 0.2476 + 3.9005 [FA] (R^2: 0.9970) with the linear range from 0.25 to 1.5 μmol/L (LOD: 0.011 μmol/L; $S/N = 3$). The second linear equation was Ip(FA) = 4.5377 + 1.2509 [FA] (R^2: 0,9957) with the linear range from 3.0 to 40 μmol/L (LOD = 0.092 μmol/L; $S/N = 3$). The proposed method was applied for the determination of FA in human serum with recovery rate from 97.3 to 101.3%.

Keywords Coal tar pitch · Differential pulse voltammetry · Folic acid · Carbonaceous material

Introduction

Folic Acid (FA) also known as vitamin B, which can be solved in water, is an important component of hematopoietic systems and a coenzyme that controls the generation of ferrohaeme. If its concentration is low in body fluids, complications such as gigantocyte, anemia, leucopenia, psychosis, and heart attacks may be observed. Vegemite and marmite are a source of folic acid (Mulinare et al. 1988). FA is particularly important for the health of pregnant women; when taken in sufficient quantities, it prevents injuries during delivery. Its deficiency may cause vertebrae and spinal injury and brain damage that occur in delivery due to the damage of nerve cells. To prevent this kind of problems, experts suggest that expectant mothers should consume either folic acid or the foods that contain folic acid. Expectant mothers are supposed to consume minimum 400 μg FA per day. This figure goes up to 600–800 μg for expectant mothers who experience nutrition problems (Milunsky et al. 1989; Medical News 1989). Moreover, FA is a natural vitamin that should be consumed by all genders (Hoegger et al. 2007).

Until now, researchers have tested many methods for the analysis of FA, which is so important for human health. Briefly, these are including UV–VIS analysis in combination with drugs, tests associated with the enzymes (Hoegger et al. 2007), chemiluminescence (Zhang et al. 2008; Anastasopoulos et al. 2007), micro-emulsion electro-kinetic chromatography (Aurora-Prado et al. 2004), fluorometry (Nagaraja et al. 2002; Yu et al. 2009), high-performance

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liquid chromatography in UV area (Amidzic et al. 2005), diode array or electrochemical analysis (Chaudhary et al. 2010; Lebiedzińska et al. 2008), liquid chromatography or mass spectroscopy through electrospray ionization (Hannisdal et al. 2009; Patring and Jastrebova 2007), and electrophorese (Uysal et al. 2010). The determination of FA in a more precise and accurate way in the body fluid, as well as in the supplementary and natural foods, that humans consume is extremely important.

At this point, it should be noted that differential pulse voltammetry is one of the most frequently used methods for the detection of many vitamins and minerals, even at lowest concentrations. Researchers have conducted many studies on this issue and showed that voltammetric methods are superior to the others.

Zhang et al. (2016) used the graphene oxide that has been modified on the carbon electrode. They recovered FA samples taken from FA supplementary tablets by 96%–100% in the buffer with pH 7.40 through the method that they have developed, and reported the detection limit as 0.5 µM. Araujo et al. (2015, 2006) determined the detection limit of FA in KCl solution as 2.67×10^{-6} M through the test that they have performed with a graphite electrode. Wei et al. (2006) used carbon nanotube in their study and they achieved to regain the FA from drug tablets by 94–97%. Majidi et al. (2011) have achieved to decrease the detection limit to 3×10^{-8} M using the carbon ceramic electrode that they have modified with polypyrrole film. Beitollahi et al. (2016) achieved to improve detection limit to 25 nM using the carbon electrodes that they have modified with ZnO–CuO. One of the most remarkable works regarding detection limit is the study published by Bandžuchová and Selešovská (2011), where they improved the detection limit to 3.88×10^{-10} M using liquid mercury silver amalgam electrode. However, the detection limit is not the only concern of these studies, in addition, the production cost of the prepared electrodes should be low and they should be produced easily.

For this reason, in our study, we focused on the determination of folic acid using the new electrode which is easy to prepare, cheap and based on differential pulse voltammetry (DPV). Nano-wrinkled layer carbonaceous electrode materials were prepared from pyrolytic carbonization of different proportions of mixtures coal tar pitch (CTP)—polystyrene (PS) composite. The electrodes were characterized by different methods such as electrochemical, microscopy, and spectroscopy methods. The electrode was used in the determination of FA by DPV. The developed method was evaluated and validated. The method was successfully applied to determine FA in human serum.

Experimental

All chemicals with the purity of analytical grade were purchased from the Merck, and Sigma-Aldrich chemical companies' local suppliers. The coal tar was purchased from Orcan Asfalt ve Yalitim Urunleri A.Ş. (Tuzla-İstanbul, Turkey). The electrochemical measurements were performed with an Ivium CompactStat under a high-purified Argon (99.999%) atmosphere at room temperature (25 ± 1 °C) with a conventional triple electrode system. The disc-shaped carbonaceous electrode was used as the working electrode. Disc electrodes were polished using Buehler micro-cloth ped (Lake Bluff, IL, USA) with 0.3, 0.1, and 0.05-micron abrasive suspension of alumina (Baikowski, USA), before experiments (Üstündağ and Erkal 2017). All polished carbonaceous electrodes were cleaned for 6 min, in an ultrasonic cleaner (SK1200H, China) with the ultra-pure water and mixture of isopropyl alcohol (IPA)/acetonitrile (MeCN) solutions (1v:1v). Ultra-pure water (UPW, 18.2 MΩ cm, Human Power 1 +, S. Korea) was used in all experiments.

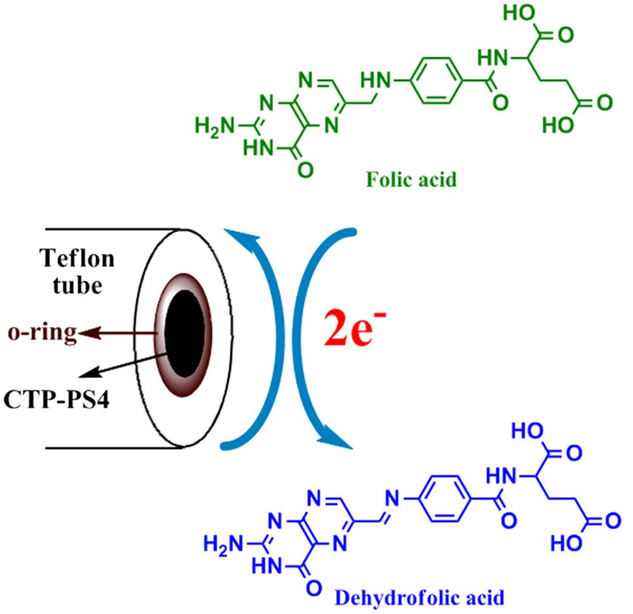
Preparation of carbonaceous electrodes

The nano-wrinkled layer carbonaceous electrode materials were prepared from pyrolytic carbonization of coal tar pitch (CTP)—polystyrene (PS) mixture. The raw mixtures of 1:9, 2:8, 3:7, 5:5, and 7:3 PS/CTP were carbonized in a tube furnace (Protherm, Turkey) with a heating rate of 10 °C/min at 1000 °C under nitrogen atmosphere. The carbonaceous materials were denoted as CTP-PS1 for 10% PS, CTP-PS2 for 20% PS, CTP-PS3 for 30% PS, CTP-PS4 for 50% PS, and CTP-PS5 for 70% PS. A pure coal tar pitch (CTP) electrode was synthesized from raw coal tar under the same conditions to compare with the CTP electrodes containing PS. The carbonized material was ground into fine powder in a mill (Retcsch/PM100 planetary ball mill, Germany) for 1 h under 500 rpm. These powders were compressed to produce disc pellets of 10 mm diameter. The small amount of *Cedrus libani* resin was used as a binder. The disc electrodes were dried in an oven at 55 °C under vacuum for 6 h (Üstündağ and Erkal 2017).

The disc electrodes were placed in the Teflon tube. The surface area of carbonaceous disc electrodes was adjusted to 0.072 cm^2 with an o-ring. Glassy carbon electrode (BAS, MF-2012) was used as compare electrode. Schematic diagram of the electrocatalytic oxidation of FA on the carbonaceous electrode system is given in Scheme 1 (Manoj et al. 2012).

Characterization of carbonaceous electrodes

The carbonaceous materials were characterized by electrochemical methods (Ivium CompactStat, Netherlands) such as CV and EIS. The electrode materials were characterized



Scheme 1 Schematic diagram of electrocatalytic oxidation of FA on the carbonaceous electrode

with SEM (Zeiss-Evo, Germany). CTP-PS4 electrode was characterized by IR (Bruker/Tensor-27, Germany).

Electrochemical applications of carbonaceous electrodes

A comparison of DPVs for FA on carbonaceous electrodes containing different amounts of PS (10% PS, 20% PS, 30% PS, 50% PS, and 70% PS) was investigated. The measurements were carried out in 0.1 M PBS solution (pH 7). Cyclic voltammograms (CVs) at different scan rates (10–500 mV/s) for FA were performed in the buffer solution. The DPV calibration voltammograms of FA exhibited a linear response in the range from 0.25 to 40 µmol/L. The accuracy of the method was investigated as intra-day and inter-day accuracy. The method was applied for the determination of FA in human serum.

Results and discussion

CTP, CTP-PS1, CTP-PS2, CTP-PS3, CTP-PS4, and CTP-PS5 electrodes were characterized by CV and EIS. CVs of 1 mM $K_4Fe(CN)_6/K_3Fe(CN)_6$ in 0.1 M KCl on the electrodes are given in Fig. 1a. Anodic peak current of the redox probe on the electrodes was compared. The maximum peak current of the redox probe was obtained on CTP-PS4 surface as 58.5 µA. The other peak currents of the redox probe on GC, CTP, CTP-PS1, CTP-PS2, CTP-PS3, and CTP-PS5 were calculated as 18.2, 26.1, 28.4, 32.5, 45.3, and 52.5 µA, respectively.

Charge transfer resistance (Rct) of the redox probe on same electrodes was investigated by EIS [frequency range is from 100 kHz to 0.2 Hz with 10 mV wave amplitude at a DC potential of 445 mV for 1 mM $K_3Fe(CN)_6$ and 1 mM $K_4Fe(CN)_6$ redox probe]. The Nyquist plots of the redox couple on the electrodes are given in Fig. 1b. These curves were fitted as Warburg-effected, diffusion-controlled CPE equivalent electrical circuit. The Rct values of the redox probe on GC, CTP, CTP-PS1, CTP-PS2, CTP-PS3, CTP-PS4, and CTP-PS5 electrodes were calculated as 3.04, 2.08, 1.24, 0.97, 0.65, 0.43, and 0.55 kΩ, respectively. The electron transfer rate of the redox couple was found as being maximum accelerated at CTP-PS4 surface. The EIS and CV results have been compatible with each other.

The stability of the CTP-PS4 disc electrode was investigated via behavior of the redox couple by CV in which the electrode was kept in an open atmosphere. Figure 1c shows the redox couple voltammogram in 0.1 KCl on CTP-PS4 electrode when it was kept in an open atmosphere for 7 days. Count of use of the electrode was checked with the same redox couple (Fig. 1d). It was concluded that the surface was stable and could be used at least 20 times.

The carbonaceous electrodes were characterized by scanning electron microscopy (SEM). The SEM images of CTP, CTP-PS1, CTP-PS2, and CTP-PS3 are given in Fig. 2.

The compact stacking of coal tar is shown Fig. 2a. The image of carbonaceous material (Fig. 2b) has changed with the addition of PS (10%). The wrinkled structure of carbonaceous material has been obtained in CTP-PS2 (Fig. 2c). Furthermore, CTP-PS3 (Fig. 2d) image was flatter than the other specimens. SEM imaging of the CTP-PS4 is given in Fig. 3a. The image of CPT-PS4 resembles a few layers of graphene oxide. We expected that the electrochemical properties of the carbonaceous material which is separated into its layers were high. Wrinkled layers increased the surface area of the electrode. Hence, the electrode gained a high electrocatalytic effect. This significant increase in electrocatalytic effect was confirmed by CV and EIS measurements.

CTP-PS4 carbonaceous materials were characterized by infrared (IR) spectroscopy. The IR spectrum of CPT-PS4 is given in Fig. 3b.

In Fig. 3b, IR spectrum of the material acquired at 450–4000 cm^{-1} range is presented. The spectrum shows a broad peak at nearly 3300–3500 cm^{-1}, which refers to the hydrogen bonding affected by hydroxyl stretch of the trace hydroxyl group. The aromatic and aliphatic symmetric and asymmetric stretching of –CH appear in 3000–3100 cm^{-1} and 2800–2950 cm^{-1}, respectively. The aromatic C–H deformation bands are observed at 600–900 cm^{-1}. The spectrum has various bands at between 1450 and 1650 cm^{-1} for the aromatic ring deformation. The peaks of between 1300 and

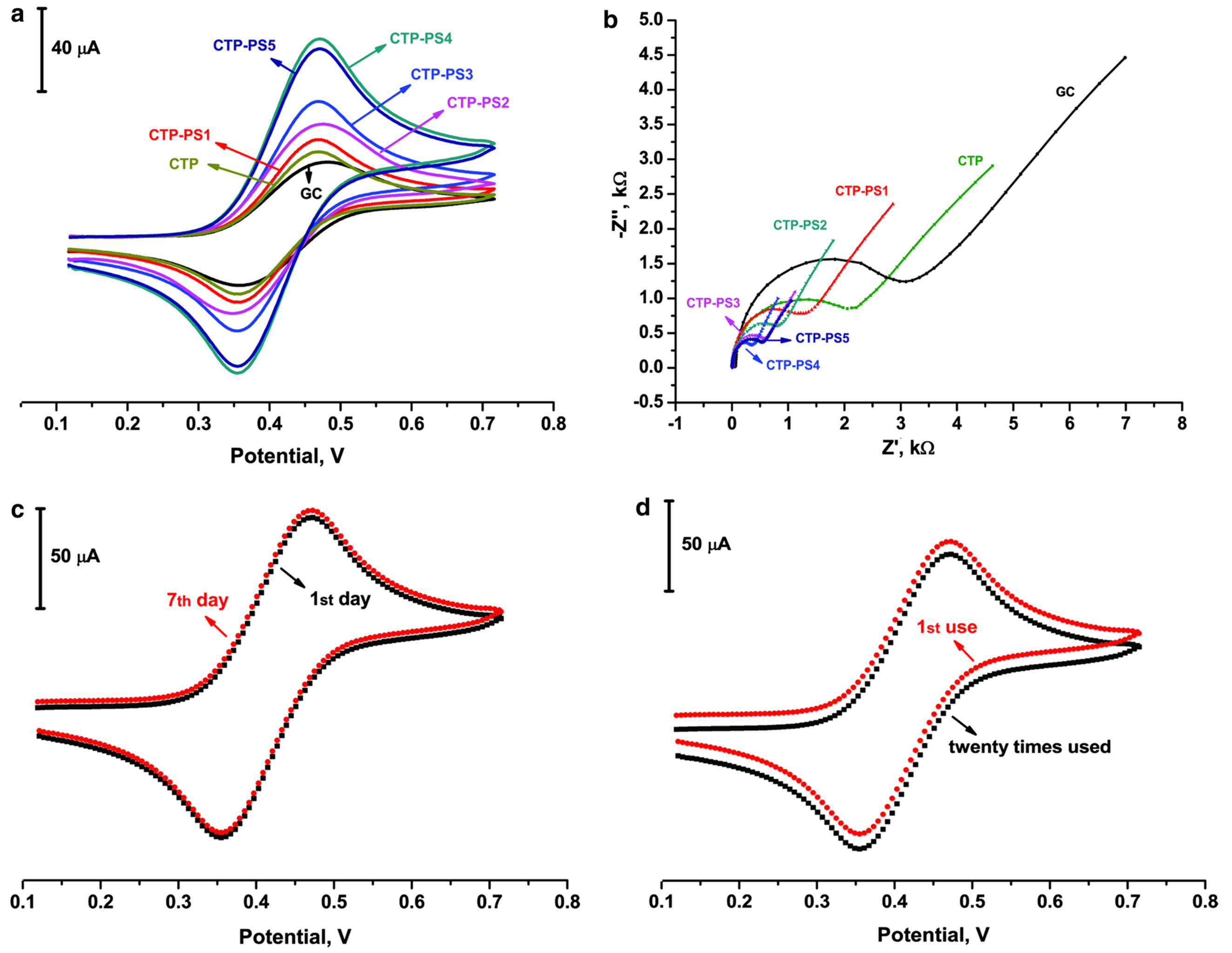


Fig. 1 **a** CVs of 1 mM $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ in 0.1 M KCl on GC, CTP, CTP-PS1, CTP-PS2, CTP-PS3, CTP-PS4, and CTP-PS5 electrodes, scan rate is 200 mV/s, vs. Ag/AgCl/KClsat and **b** Nyquist plots of 1 mM $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ in 0.1 M KCl on CTP, CTP-PS1, CTP-PS2, CTP-PS3, CTP-PS4, and CTP-PS5 electrodes, scan rate is 200 mV/s, vs. Ag/AgCl/KClsat. **c** CVs of 1 mM $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ on CTP-PS4 in 0.1 M KCl with a scan rate of 200 mV/s, vs. Ag/Ag^+ (0.1 M) for **c** stability test of the CTP-PS4, and **d** count of use of the CTP-PS4 when it is kept in open atmosphere for 1 week

1450 cm^{-1} correspond to the aliphatic –CH bending. The peak at 1700 cm^{-1} refers to the C=O-stretching vibration on the carbonaceous material (Erkal et al. 2016; Abuilaiwi et al. 2010; Tehrani et al. 2013).

DPVs of 10 µmol/L FA on different carbonaceous electrodes (CTP, CTP-PS1, CTP-PS2, CTP-PS3, CTP-PS4, and CTP-PS5) are given in Fig. 4a. The maximum peak current of FA was obtained on the surface of CTP-PS4 electrode. The electron transfer rate of FA on CTP-PS4 electrode has dramatically accelerated. LSVs of FA on CTP-PS4 electrode under different scan rates (0.25–40 mV/s) were performed in the buffer solution. The LSVs are given in Fig. 4b.

The electron transfer kinetics of FA on CTP-PS4 was diffusion controlled. The peak current of FA by CV was shown linearly proportional to the square root of scan rates. The calibration DPVs of 0.25–40 µmol/L FA on CTP-PS4 and their calibration curve are given in Fig. 5.

The calibration curve has had two linear zones. The first linear equation for FA was Ip(FA) = 0.2476 + 3.9005 [FA] (R^2: 0,9970) with the linear range of 0.25 µmol/L to 1.5 µmol/L. Furthermore, the second equation was Ip(FA) = 4.5377 + 1.2509 [FA] (R^2: 0,9957) with the linear range of 3.0–40 µmol/L. Limit of detection (3σ) of the first linear zone was 0.011 µmol/L and the second linear zone was 0.092 µmol/L. Calibration sensitivities were calculated as 3.90 and 1.25 µA/µM, respectively. The developed method gave good results according to other reported detection limits in the literature. Comparison of the developed method and other methods is given in Table 1.

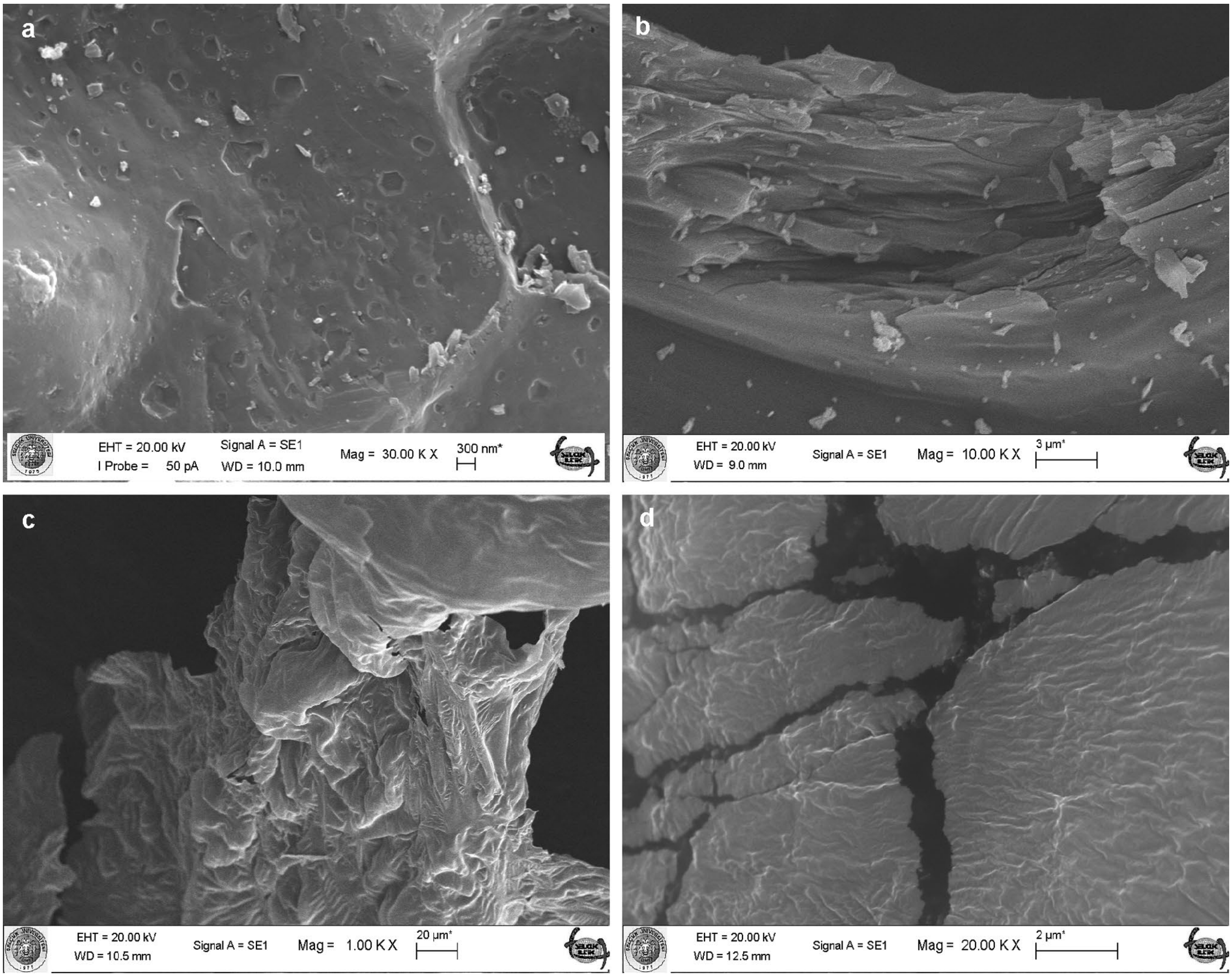


Fig. 2 SEM images of the CTP (**a**), CTP-PS1 (**b**), CTP-PS2 (**c**), and CTP-PS3 (**d**)

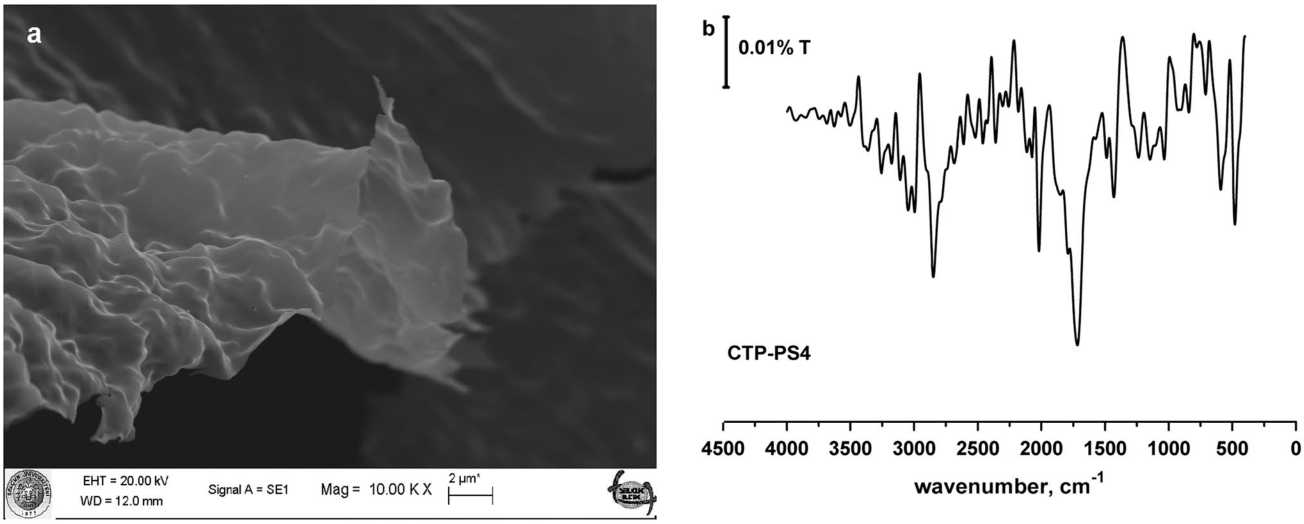


Fig. 3 SEM imaging (**a**) and IR spectrum (**b**) of the CTP-PS4

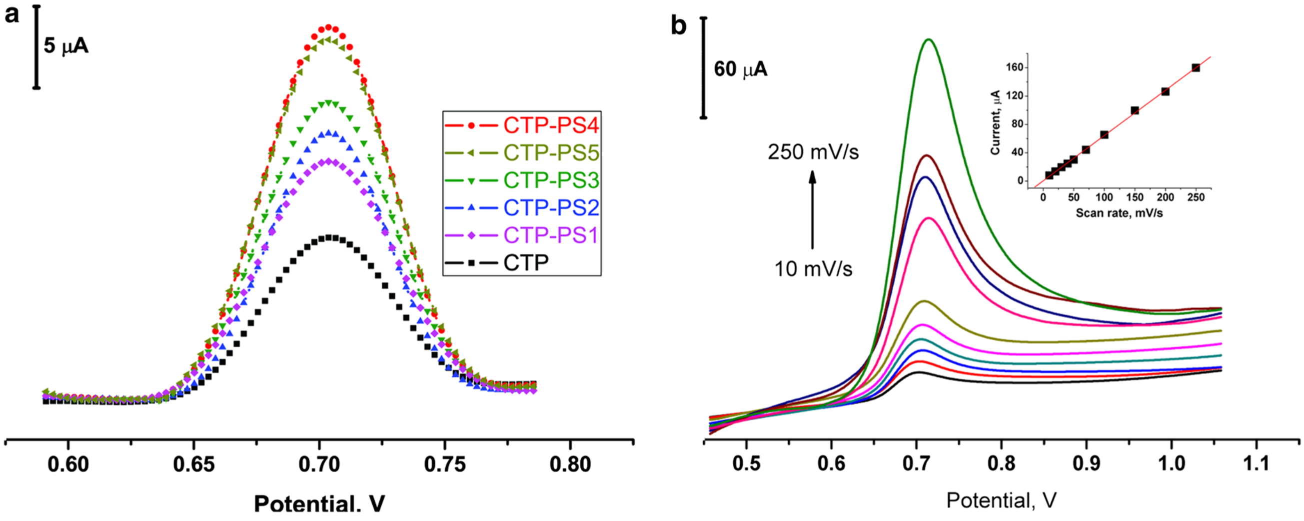


Fig. 4 **a** DPVs of 10 µmol/L FA on different carbonaceous electrode (CTP, CTP-PS1, CTP-PS2, CTP-PS3, CTP-PS4, and CTP-PS5 (scan rate is 20 mV/s toward the positive potential with a pulse amplitude of 25 mV, and the pulse rate is 0.5 s, under a pulse width of 60 ms for a holding time of 2 s). **b** LSVs of 1 mmol/L FA on CTP-PS4 electrode under different scan rates vs. Ag/AgCl reference electrode

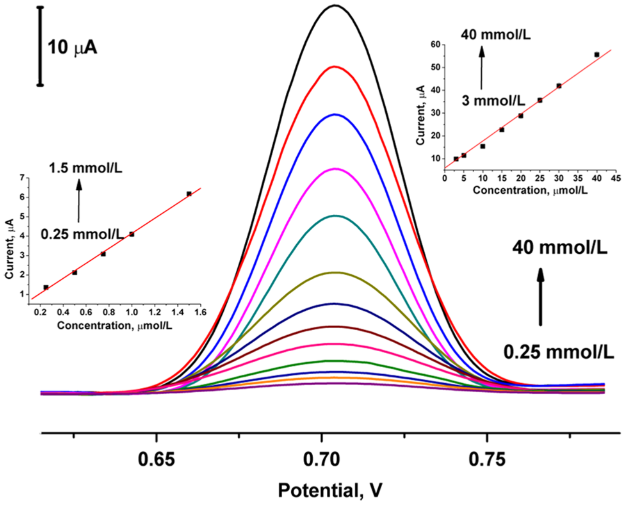


Fig. 5 DPVs of 0.25–40 µmol/L FA on CTP-PS4 and their calibration curves (inset)

Three different concentrations of FA (0.5, 7.5, and 21.2 µmol/L) in the linear response zone were measured as five independent series on the same day for intra-day precision (RSD). In addition, for inter-day precision, measurements were performed on seven consecutive days with five measurements in every series. The RSD % and accuracy % results are given in Table 2. The RSD was $\leq 4.00\%$ for both intra-day and inter-day precision. The accuracy of the method was calculated as $\leq +4.00\%$ and $\geq 2.00\%$ for intra-day and inter-day accuracy.

The influences of some molecules and ions on the peak currents of 1 µmol/L FA in 0.1 M PBS (pH 7.0) are given in Table 3. In the table, signal changes are presented for 1000 µmol/L of interference species including dopamine (DA), uric acid (UA), L-alanine, D-glucose, Na^+, and Mg^{2+}.

The proposed method was applied for the determination of FA in human serum. The results are given in Table 4. FA (1.5, 5, 10, and 15 µmol/L) was spiked in commercial human serum samples. The recovery percentages values of the developed standard addition method for 1.5, 5, 10, and 15 µmol/L FA were found as 101.3, 98.6, 97.3, and 99.1, respectively.

Conclusions

A simple and efficient a novel carbonaceous electrode was fabricated and adapted to the FA determination. The CTP-PS4 electrode exhibited the most electrocatalytic effect to FA. A novel analysis method for FA was developed successfully. Moreover, the electrode showed good reproducibility, repeatability, and stability even in the presence of interference groups. The obtained linear range calibration plot of folic acid vs. oxidation peak current resulted in two linear zones. The first linear zone equation for FA was Ip(FA) = 0.2476 + 3.9005 [FA] (R^2: 0,9970) with the linear range from 0.25 to 1.5 µmol/L (LOD: 0.011 µmol/L; $S/N = 3$). The other equation was Ip(FA) = 4.5377 + 1.2509 [FA] (R^2: 0,9957) with the linear range from 3.0 to 40 µmol/L (LOD = 0.092 µmol/L; $S/N = 3$). The developed methods were applied to commercial human serum, and the analytical recovery of FA added to samples was between $\geq 97.3\%$ and ≤ 101.3.

Table 1 Response of various voltammetric nanosensors for FA

Electrode	Technique	Calibration range (µmol/L)	LOD (µmol/L)	Refs.
AuNPs–β–CD–Graphene	SWV	1–10	0.027	Arvand et al. (2017)
Au-ERGO/CILE	Amperometry	0.01–50	0.027	Wang et al. (2015)
POMANS-MWCNT/GPE	LSV	0.5–68	0.113	Rajabi and Noroozifar (2017)
ZnSe@ZnS	CV	0.012–0.096	0.005	Mir et al. (2017)
Mn-SnO_2/GCE	DPV	0.5–900	0.079	Lavanya et al. (2016)
POMA-Au/GCE	DPV	0.5–900	0.090	Sangamithirai et al. (2018)
ZrO_2 NPs/CPE	DPV	10–2000	0.089	Mazloum-Ardakani et al. (2010)
MCPE/Fe-MWCNTs	DPV	0.009–9	0.002	D'Souza et al. (2017)
(PEI/P2Mo16V2-rGO)4	DPV	0.01–800	0.0003	Xu et al. (2017)
GC/CTP-PS4	DPV	0.25–1.5 and 3.0–40.0	0.011 and 0.092	This work

Table 2 Precision and accuracy results of the method ($N=5$)

Added (µmol/L)	Intra-day			Inter-day		
	Found value (µmol/L)	Precision (%)	Accuracy (%)	Found value (µmol/L)	Precision (%)	Accuracy (%)
0.5	0.52 ± 0.02	3.85	+ 4.00	0.49 ± 0.01	2.04	2.00
7.5	7.7 ± 0.2	2.60	+ 2.67	7.4 ± 0.2	2.70	− 1.33
21.2	20.8 ± 0.2	0.96	− 1.89	21.5 ± 0.3	1.40	+ 1.41

Table 3 Interferences of different species on the detection 1 µmol/L FA as peak signal change %

Interfering groups	Concentration (µmol/L)	Signal change (%) of FA
DA	100	− 1.27
UA	100	− 2.63
L-Alanine	100	1.37
D-Glucose	100	− 3.01
Na^+	100	1.15
Mg^{2+}	100	0.96

Table 4 Analytical recovery of FA added to human serum samples ($N=5$)

Sample	Added (µmol/L)	Detected by DPV (µmol/L)	Recovery (%)
Human serum	1.5	1.52	101.3
	5	4.93	98.6
	10	9.73	97.3
	15	14.87	99.1

References

Abuilaiwi FA, Laoui T, Al-Harthi M, Atieh MA (2010) Modification and functionalization of multiwalled carbon nanotube (MWCNT) via FISCHER esterification. Arab J Sci Eng 35:37–48. https://doi.org/10.13140/2.1.3447.3925

Amidzic R, Brboric J, Cudina O, Vladimirov S (2005) RP-HPLC Determination of vitAMins B1, B3, B6, folic acid and B12 in multivitAMin tablets. J Serb Chem Soc 70:1229–1235. https://doi.org/10.2298/JSC0510229A

Anastasopoulos P, Mellos T, Spinou M, Tsiaka T, Timotheou-Potamia M (2007) Chemiluminometric and fluorimetric determination of folic acid. Anal Lett 40:2203–2216. https://doi.org/10.1080/00032710701567022

Araujo EG, Fernandes NS, Solon LGS, Aragao CFS, Huitle CAM (2015) Voltammetric determination of folic acid using a graphite paste electrode. Electroanalysis 27:398–405. https://doi.org/10.1002/elan.201400475

Arvand M, Pourhabib A, Giahi M (2017) Square wave voltammetric quantification of folic acid, uric acid and ascorbic acid in biological matrix. J Pharm Anal 7:110–117. https://doi.org/10.1016/j.jpha.2017.01.002

Aurora-Prado MS, Silva CA, Tavares MF, Altria KD (2004) Determination of folic acid in tablets by microemulsion electrokinetic chromatography. J Chromatogr A 1051:291–296. https://doi.org/10.1016/j.chroma.2004.08.042

Bandžuchová L, Selešovská R (2011) Voltammetric determination of folic acid using liquid mercury free silver amalgam electrode. Acta Chim Slov 58:776–784

Beitollahi H, Ivari SG, Torkzadeh-Mahani M (2016) Voltammetric determination of 6-thioguanine and folic acid using a carbon paste electrode modified with ZnO–CuO nanoplates and modifier. Mater Sci Eng C 69:128–133. https://doi.org/10.1016/j.msec.2016.06.064

Chaudhary A, Wang J, Prabhu S (2010) Development and validation of a high-performance liquid chromatography method for the simultaneous determination of aspirin and folic acid from nanoparticulate systems. Biomed Chromatogr 24:825–919. https://doi.org/10.1002/bmc.1386

D'Souza OJ, Mascarenhas RJ, Satpati AK, Detriche S, Mekhalif Z, Delhalle J, Dhason A (2017) High electrocatalytic oxidation of folic acid at carbon pasteelectrode bulk modified with iron nanoparticle-decorated multiwalled carbon nanotubes and its application in food and pharmaceutical analysis. Ionics 23:201–212. https://doi.org/10.1007/s11581-016-1806-y

Erkal A, Aşık İ, Yavuz S, Kariper A, Üstündağ Z (2016) Biosensor application of carbonaceous nanocoil material: preparation, characterization, and determination of dopamine and uric acid in the presence of ascorbic acid. J Electrochem Soc 163:H269–H277. https://doi.org/10.1149/2.0231605jes

Hannisdal R, Ueland PM, Svardal A (2009) Liquid chromatography–tandem mass spectrometry analysis of folate and folate catabolites in human serum. Clin Chem 55:1147–1154. https://doi.org/10.1373/clinchem.2008.114389

Hoegger D, Morier P, Vollet C, Heini D, Reymond F, Rossier JS (2007) Disposable microfluidic ELISA for the rapid determination of folic acid content in food products. Anal Bioanal Chem 387:267–275. https://doi.org/10.1007/s00216-006-0948-6

Lavanya N, Fazio E, Neri F, Bonavita A, Leonardi SG, Neri G, Sekar C (2016) Electrochemical sensor for simultaneous determination of ascorbic acid, uric acid and folic acid based on Mn–SnO_2 nanoparticles modified glassy carbon electrode. J Electroanal Chem 770:23–32. https://doi.org/10.1016/j.jelechem.2016.03.017

Lebiedzińska A, Dabrowska M, Szefer P (2008) High-performance liquid chromatography method for the determination of folic acid in fortified food products. Toxicol Mech Methods 18:463–467. https://doi.org/10.1080/15376510701623870

Majidi MR, Dastangoo H, Hasannejad M, Malakouti J (2011) Voltammetric determination of folic acid with a overoxidized polypyrrole film modified sol–gel carbon ceramic electrode. Int J Polym Anal Charact 16:486–495. https://doi.org/10.1080/1023666X.2011.600837

Manoj D, Kumar DR, Santhanalakshmi J (2012) Impact of CuO nanoleaves on MWCNTs/GCE nanocomposite film modified electrode for the electrochemical oxidation of folic acid. Appl Nanosci 2:223–230. https://doi.org/10.1007/s13204-012-0093-9

Mazloum-Ardakani M, Beitollahi H, Amini MK, Mirkhalaf F, Abdollahi-Alibeik M (2010) New strategy for simultaneous and selective voltammetric determination of norepinephrine, acetaminophen and folic acid using ZrO_2 nanoparticles-modified carbon paste electrode. Sens Actuators B Chem 151:243–249. https://doi.org/10.1016/j.snb.2010.09.011

Medical News (1989) Extra folate for men may reduce birth defects. In: Primary care, diet and nutrition from med page today

Milunsky A, Jick H, Jick SS, Bruell CL, MacLaughlin DS, Rothman KJ, Willett W (1989) Multivitamin/folic acid supplementation in early pregnancy reduces the prevalence of neural tube defects. J Am Med Assoc 262:2847–2852. https://doi.org/10.1001/jama.1989.03430200091032

Mir IA, Rawat K, Solanki PR, Bohidar HB (2017) ZnSe core and ZnSe@ZnS core–shell quantum dots as platform for folic acid sensing. J Nanopart Res 19:260–270. https://doi.org/10.1007/s11051-017-3942-3

Mulinare J, Cordero JF, Erickson JD, Berry RJ (1988) Periconceptional use of multivitamins and the occurrence of neural tube defects. J Am Med Assoc 260:3141–3145. https://doi.org/10.1001/jama.1988.03410210053035

Nagaraja P, Vasantha RA, Yathirajan HS (2002) Spectrophotometric determination of folic acid in pharmaceutical preparations by coupling reactions with iminodibenzyl or 3-aminophenol or sodium molybdate–pyrocatechol. Anal Biochem 307:316–321. https://doi.org/10.1016/S0003-2697(02)00038-6

Patring JD, Jastrebova JA (2007) Application of liquid chromatography–electrospray ionisation mass spectrometry for determination of dietary folates: effects of buffer nature and mobile phase composition on sensitivity and selectivity. J Chromatogr A 1143:72–82. https://doi.org/10.1016/j.chroma.2006.12.079

Rajabi H, Noroozifar M (2017) New synthesis of poly ortho-methoxyaniline nanostructures and its application to construct modified multi-wall carbon nanotube/graphite paste electrode for simultaneous determination of uric acid and folic acid. Mater Sci Eng C 75:791–797. https://doi.org/10.1016/j.msec.2017.02.133

Sangamithirai D, Munusamy S, Narayanan V, Stephen A (2018) Mater Sci Eng C 91:512–523. https://doi.org/10.1016/j.msec.2018.05.070

Tehrani MS, Azar PA, Namin PE, Dehaghi SM (2013) Removal of lead ions from wastewater using functionalized multiwalled carbon nanotubes with tris(2-aminoethyl)amine. J Environ Protect 4:529–536. https://doi.org/10.4236/jep.2013.46062

Üstündağ İ, Erkal A (2017) Determination of dopamine in the presence of ascorbic acid on digitonin-doped coal tar pitch carbonaceous electrode. Sens Mater 29:85–94. https://doi.org/10.18494/SAM.2017.1416

Uysal UD, Kaya EM, Tuncel M (2010) Determination of folic acid by capillary electrophoresis in various cultivated variety of lentils. Chromatographia 71:653–658. https://doi.org/10.1365/s10337-010-1555-4

Wang X, You Z, Cheng Y, Sha H, Li G, Zhu H, Sun W (2015) Application of nanosized gold and graphene modified carbon ionic liquid electrode for the sensitive electrochemical determination of folic acid. J Mol Liq 204:112–117. https://doi.org/10.1016/j.molliq.2015.01.036

Wei S, Zhao F, Xu Z, Zeng B (2006) Voltammetric determination of folic acid with a multi-walled carbon nanotube-modified gold electrode. Microchim Acta 152:285–290. https://doi.org/10.1007/s00604-005-0437-1

Xu H, Bai Z, Wang G, O'Halloran KP, Tan L, Pang H, Ma H (2017) Voltammetric determination of folic acid at physiological pHvalues by using a glassy carbon electrode modifiedwith a multilayer composite consistingof polyoxometalate ($H_8P_2Mo_{16}V_2O_{62}$) and reduced grapheneoxide and prepared via layer-by-layer self-assembly and in-situphotoreduction. Microchim Acta 184:4295–4303. https://doi.org/10.1007/s00604-017-2447-1

Yu F, Cui M, Chen F, Gao Y, Wei J, Ding Y (2009) Highly sensitive spectrofluorimetric determination of trace amounts of folic acid using a oxytetracycline-terbium(III) probe. Anal Lett 42:178–189. https://doi.org/10.1080/00032710802568663

Zhang BT, Zhao L, Lin JM (2008) Determination of folic acid by chemiluminescence based on peroxomonosulfate-cobalt(II) system. Talanta 74:1154–1159. https://doi.org/10.1016/j.talanta.2007.08.027

Zhang D, Ouyang X, Ma W, Li L, Zhang Y (2016) Voltammetric determination of folic acid using adsorption of methylene blue onto electrodeposited of reduced graphene oxide film modified glassy carbon electrode. Electroanalysis 28:312–319. https://doi.org/10.1002/elan.201500348